

# Plasma Assisted Combustion Mechanism for Small Hydrocarbons

Andrey Starikovskiy  
Nickolay Aleksandrov



PRINCETON  
University



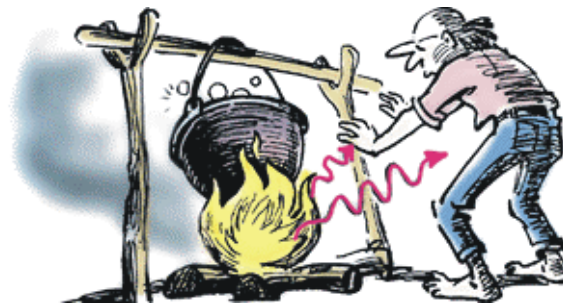
Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE <b>2015</b>		2. REPORT TYPE		3. DATES COVERED <b>00-00-2015 to 00-00-2015</b>	
4. TITLE AND SUBTITLE <b>Plasma Assisted Combustion Mechanism for Small Hydrocarbons</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Princeton University, Princeton, NJ, 08544</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>AFOSR MURI 2015 Fifth Year Review Meeting</b>					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>Same as Report (SAR)</b>	18. NUMBER OF PAGES <b>45</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

# Ignition, Combustion and Flame Control by Nonequilibrium Plasma

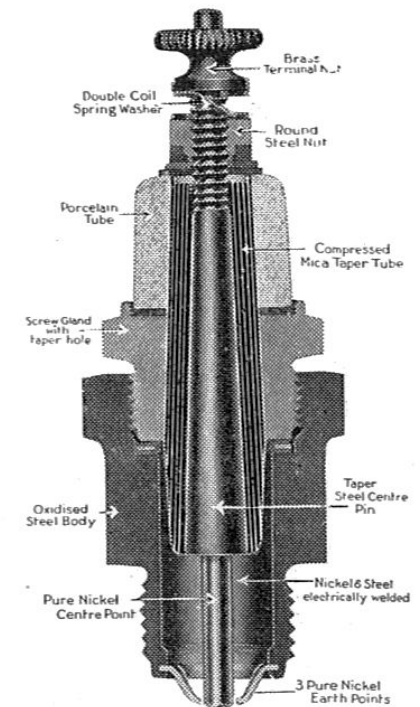


**1814 – Brande. Flame/Field Interaction**

**W.T. Brande. Phil.Trans.Roy.Soc., 1814,104, 51.**



In 1860 Étienne Lenoir used an electric spark plug in his gas engine, the first internal combustion piston engine and is generally credited with the invention of the spark plug



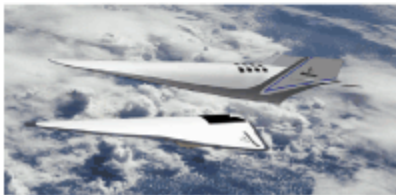
# Propulsion Efficiency and Operating Regimes for Variety of Flight Systems



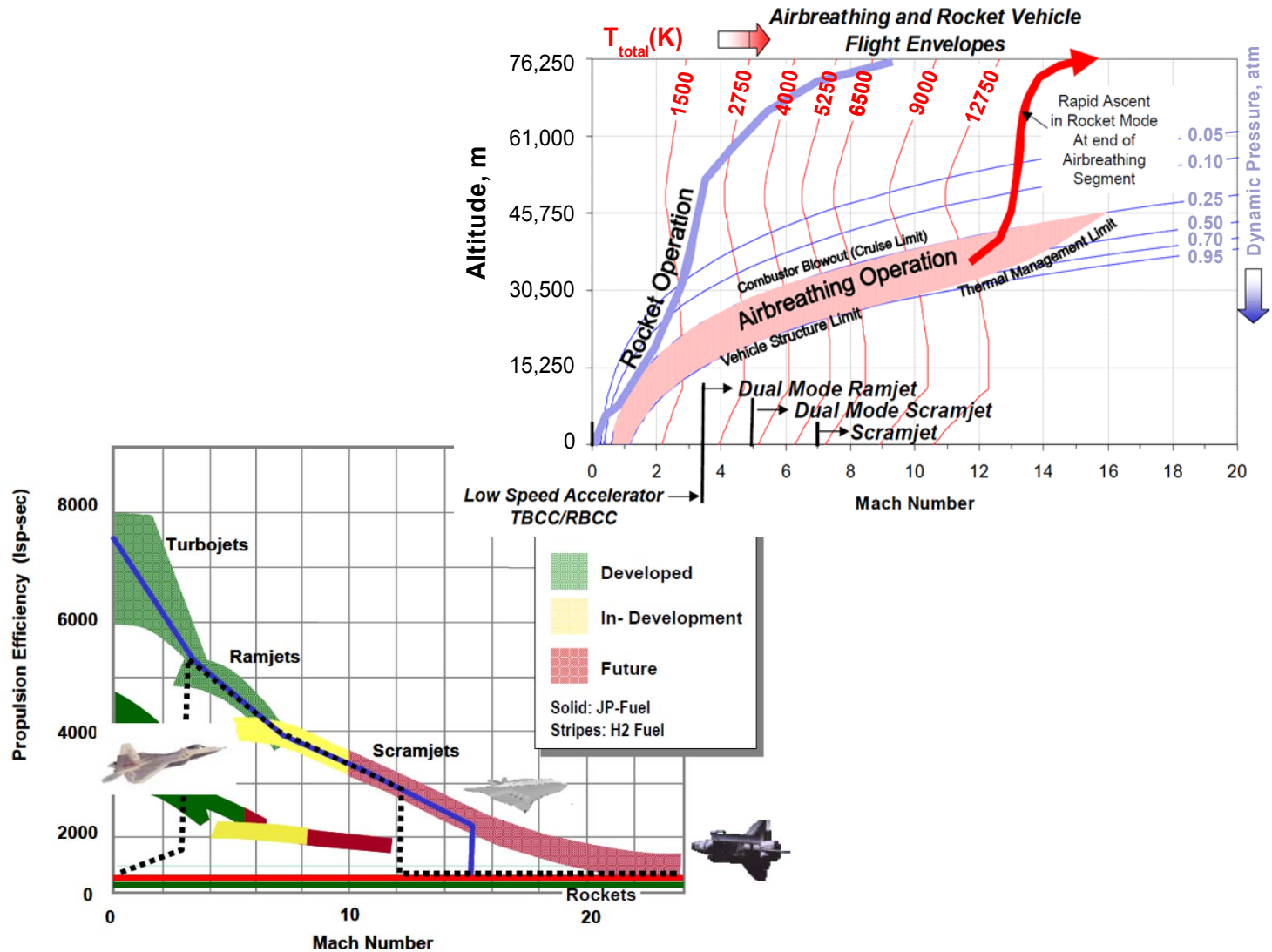
(a)



(b)

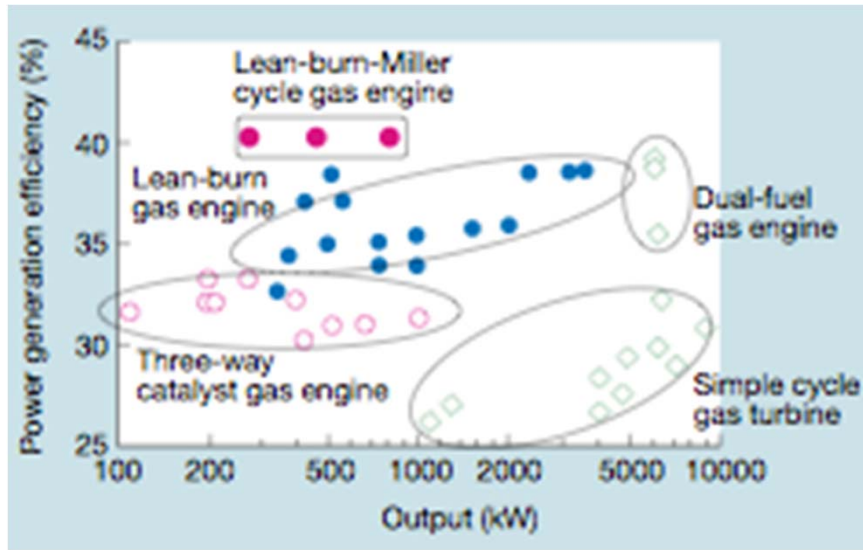


(c)

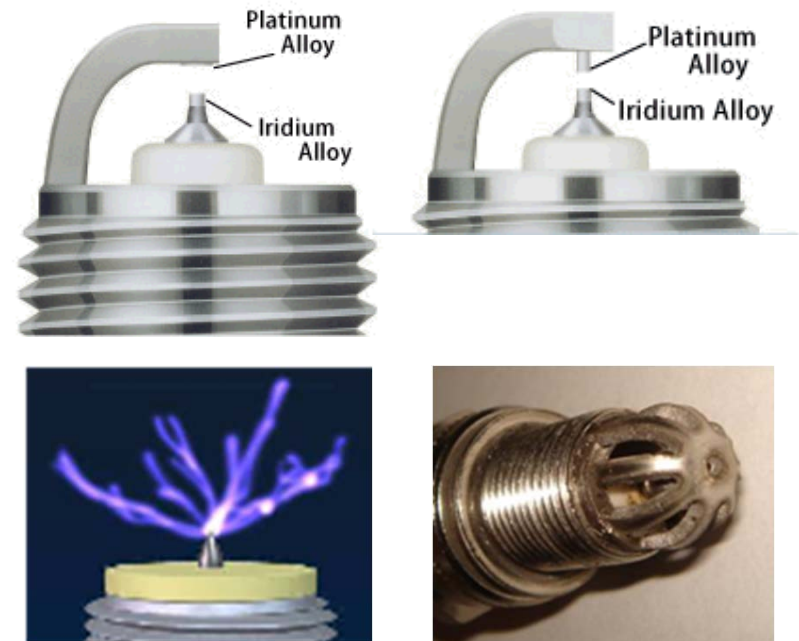
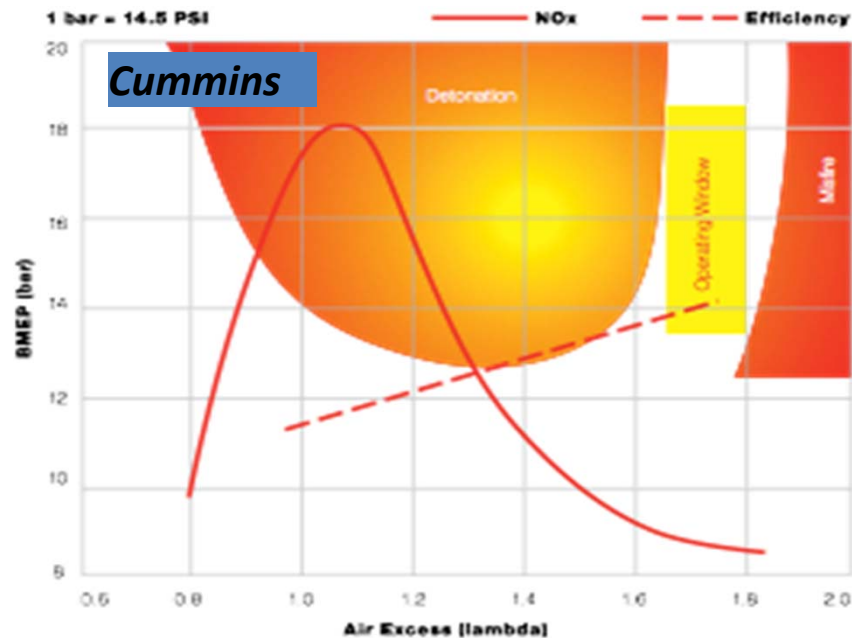




# Lean Ignition for Gas IC Engines



- Regular spark plugs  $\lambda < 1.4$
- Regular spark plugs with thin (Iridium/Platinum) electrodes  $\lambda < 1.6$
- RF, “plasma”, etc. plugs  $\lambda < 1.8$

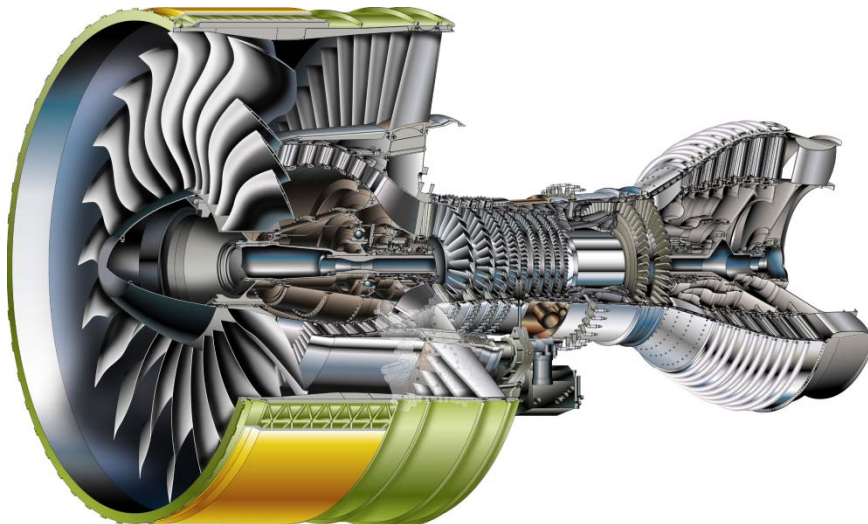
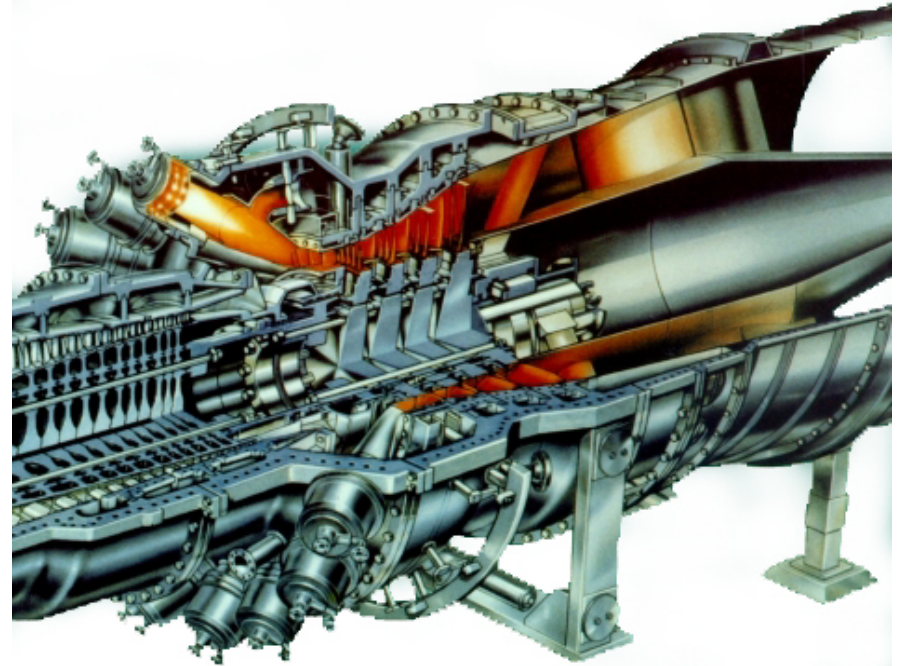


# GTE Lean Regimes

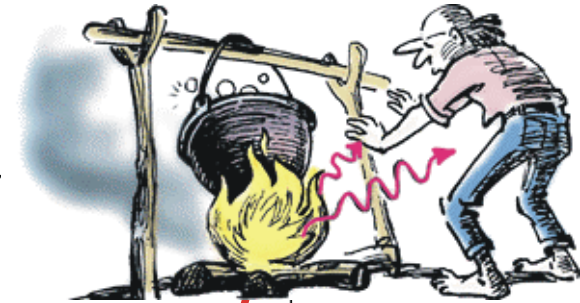
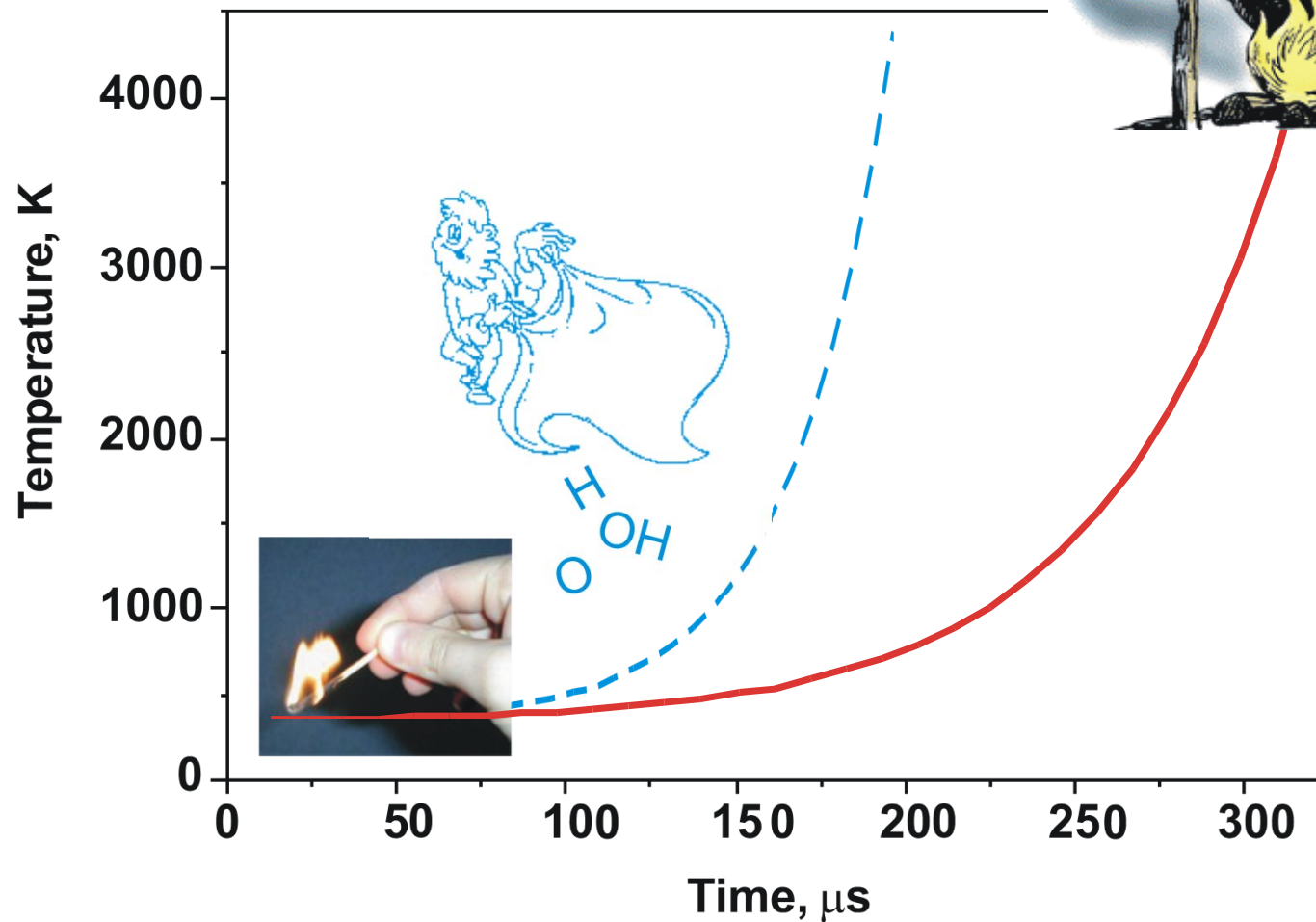
**$T = 700 - 1300 \text{ K}$**

**$P = 20 - 30 \text{ atm}$**

**$W = 10 - 1000 \text{ MW}$**



# Decreasing of Ignition Delay Time - 1994



# Kinetic Model: Previous Versions

**D.V.Zatsepin, S.M.Starikovskaia, A.Yu.Starikovskii** *Hydrogen oxidation in a stoichiometric hydrogen-air mixtures in the fast ionization wave.* Combust. Theory Modeling, 2001. V.5 pp.97-129.

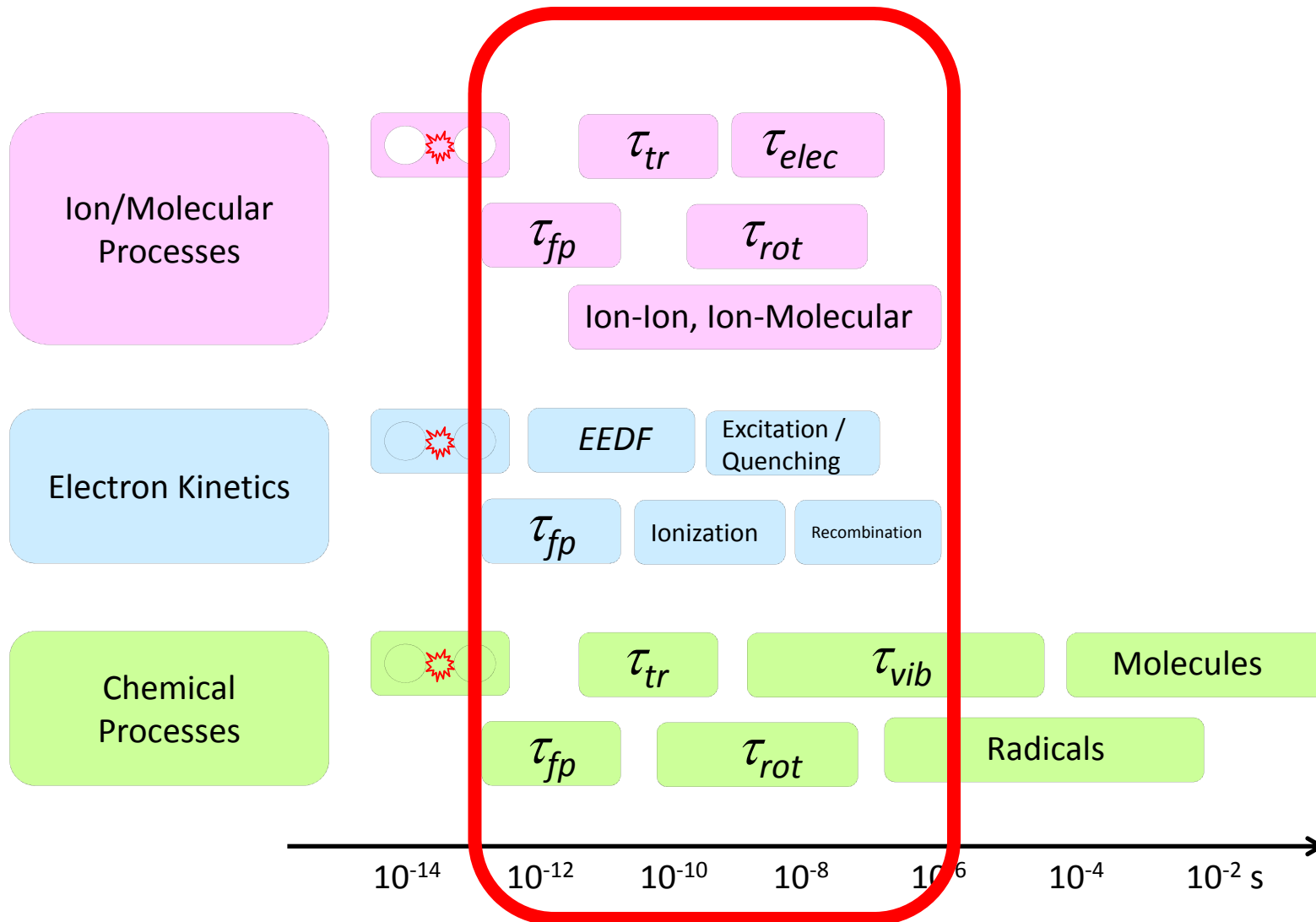
**N.A.Popov.** *Effect of a Pulsed High-Current Discharge on Hydrogen–Air Mixtures.* Plasma Physics Reports, 2008, Vol. 34, No. 5, pp. 376–391.

**I.N. Kosarev, N.L. Aleksandrov, S.V. Kindysheva, S.M. Starikovskaia , A.Yu. Starikovskii.** *Kinetics of ignition of saturated hydrocarbons by nonequilibrium plasma: C<sub>2</sub>H<sub>6</sub>- to C<sub>5</sub>H<sub>12</sub>-containing mixtures.* Combustion and Flame 156 (2009) 221–233

**A.Starikovskiy, N.Aleksandrov.** *Plasma-assisted ignition and combustion.* Progress in Energy and Combustion Science 39 (2013) 61-110

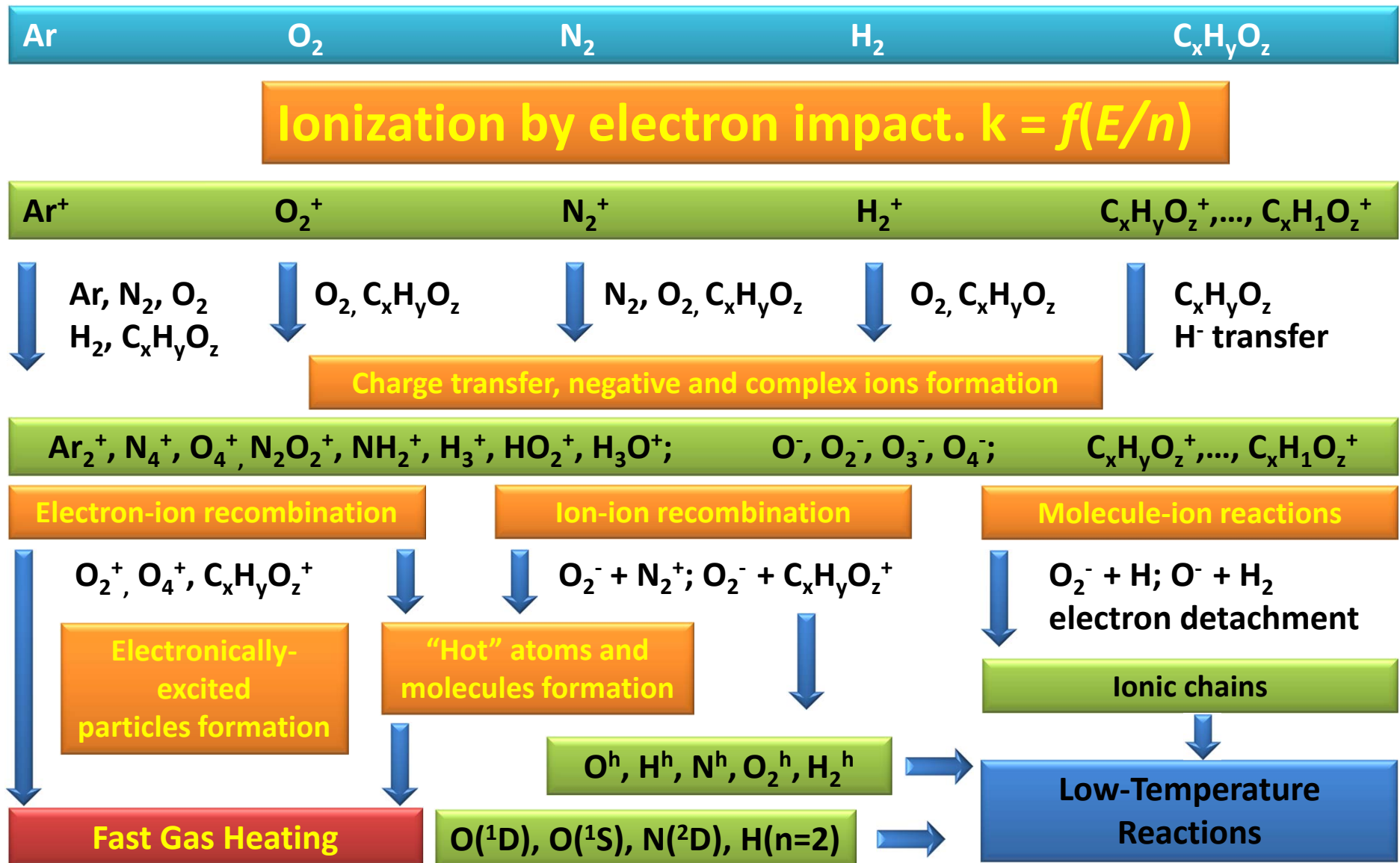
# Predictive Modeling:

## Key to Applications



# Princeton Plasma Combustion Kinetics

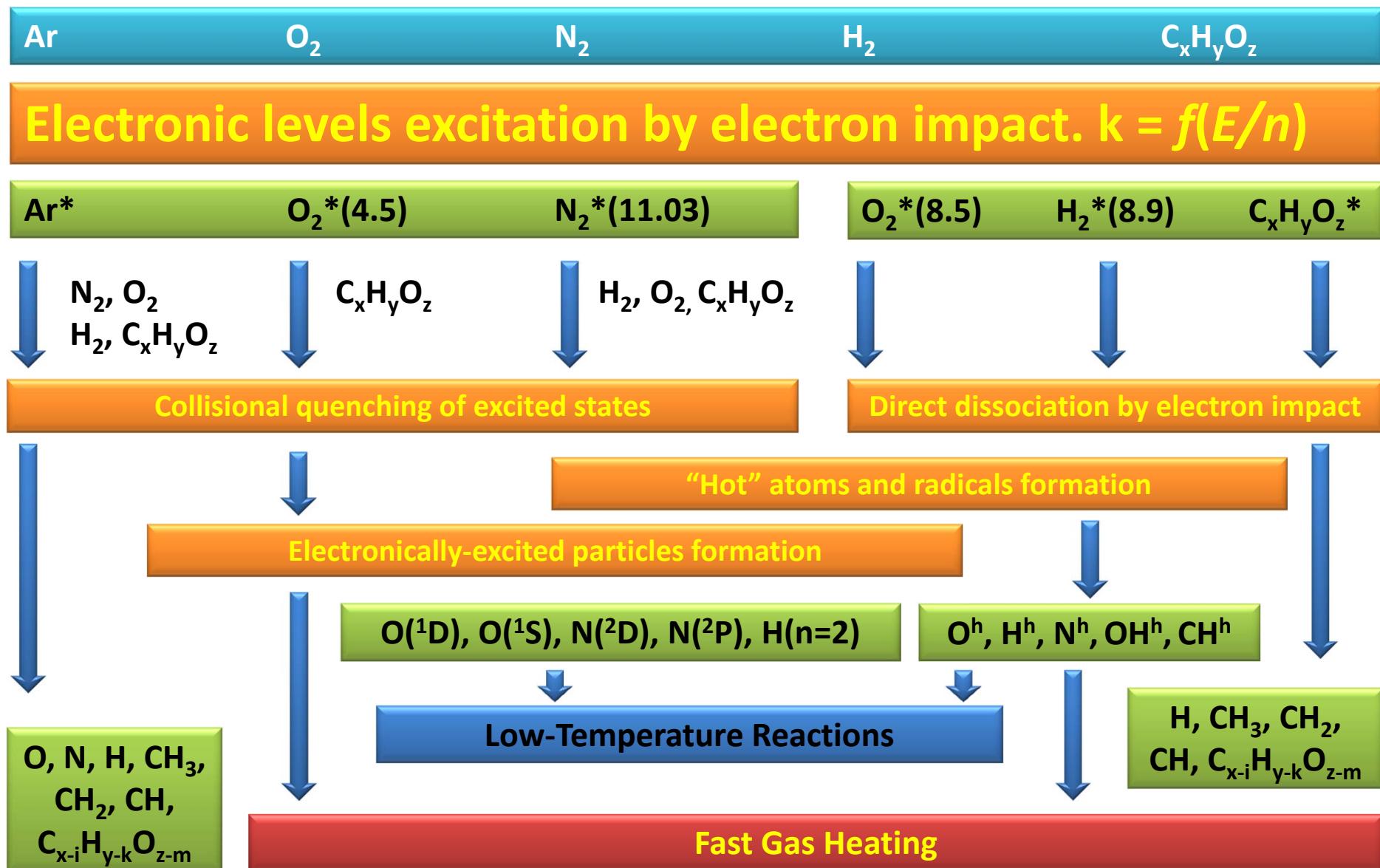
## *Major Pathways*





# Princeton Plasma Combustion Kinetics

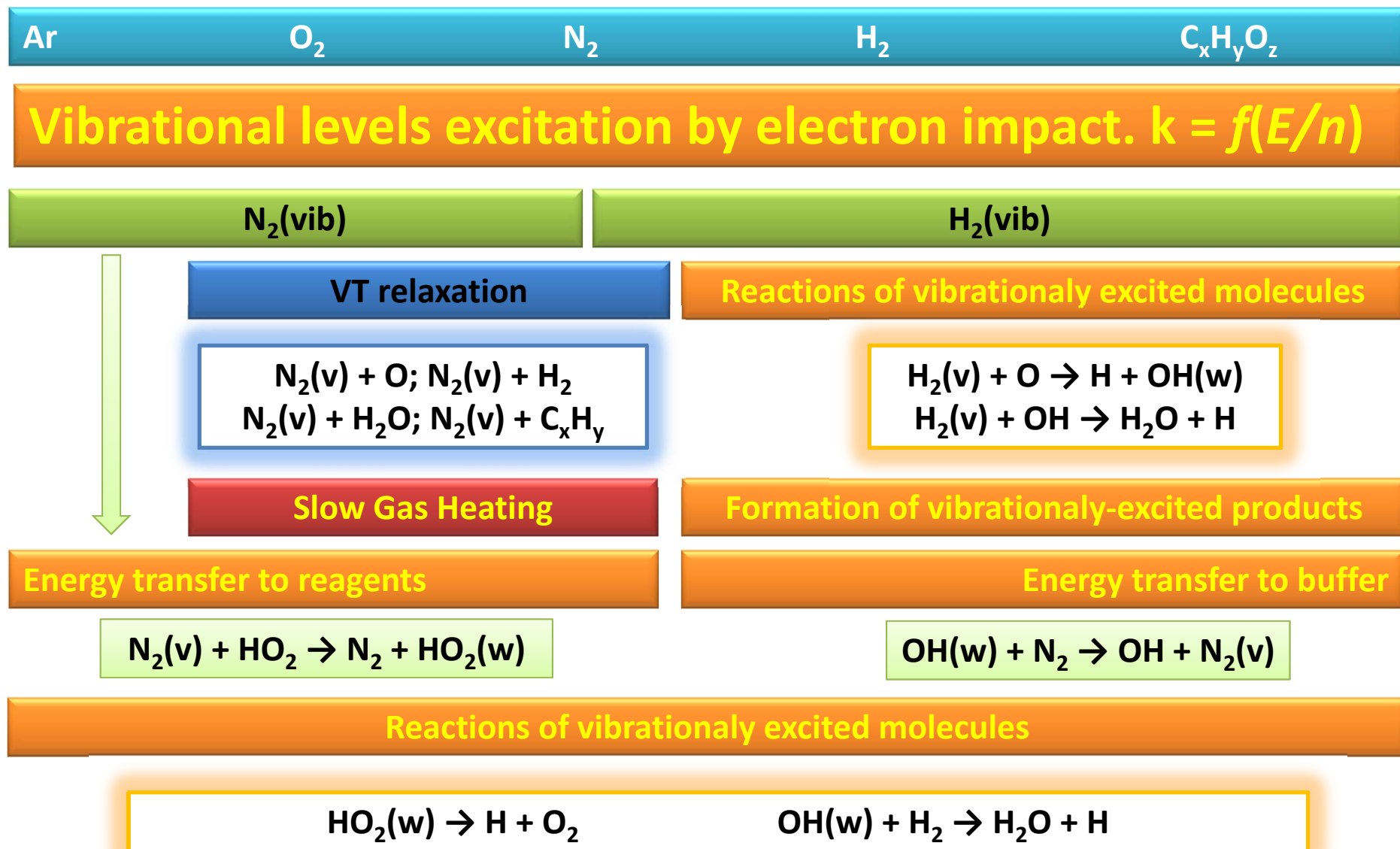
## *Major Pathways*



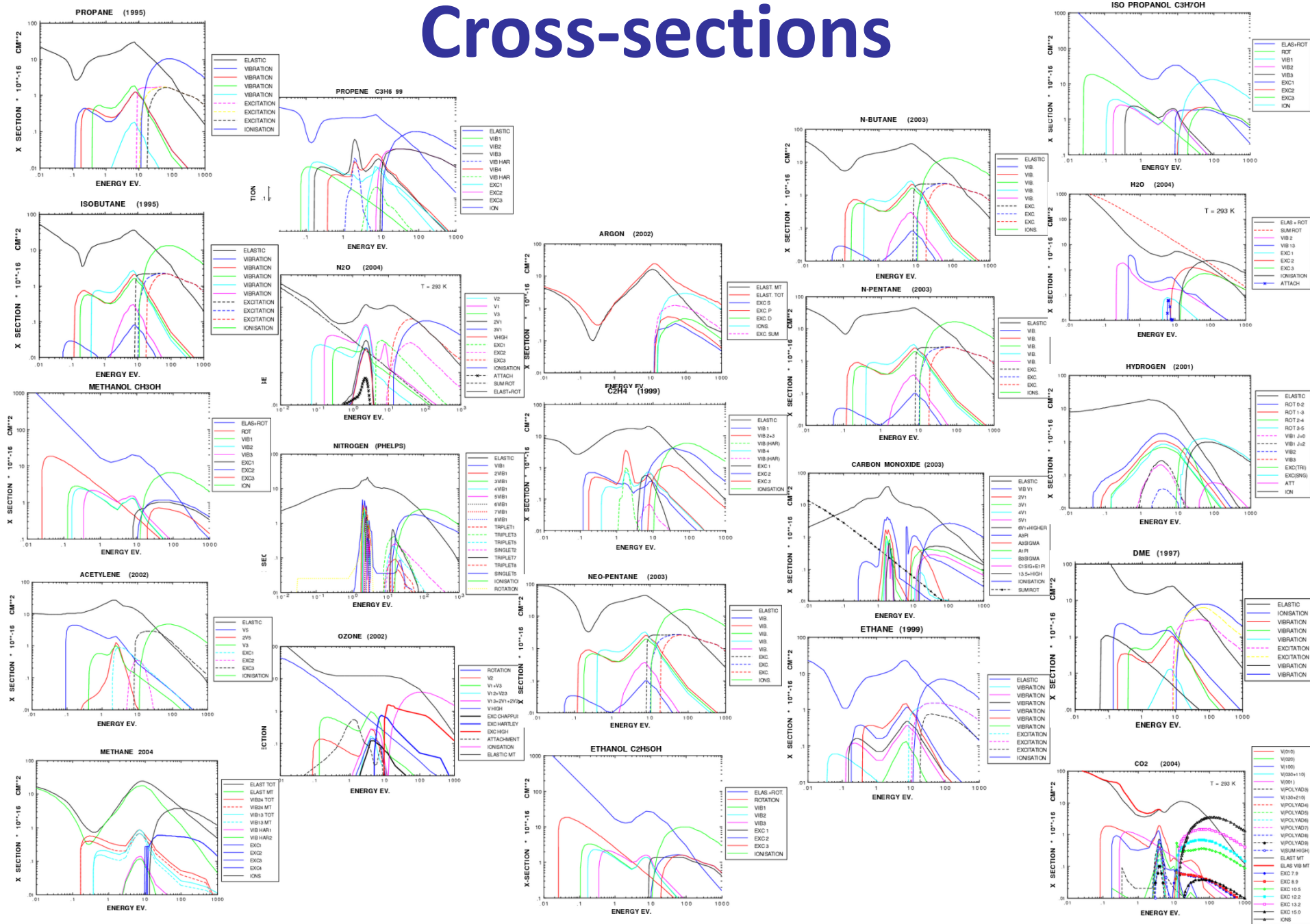


# Princeton Plasma Combustion Kinetics

## *Major Pathways*



# Cross-sections

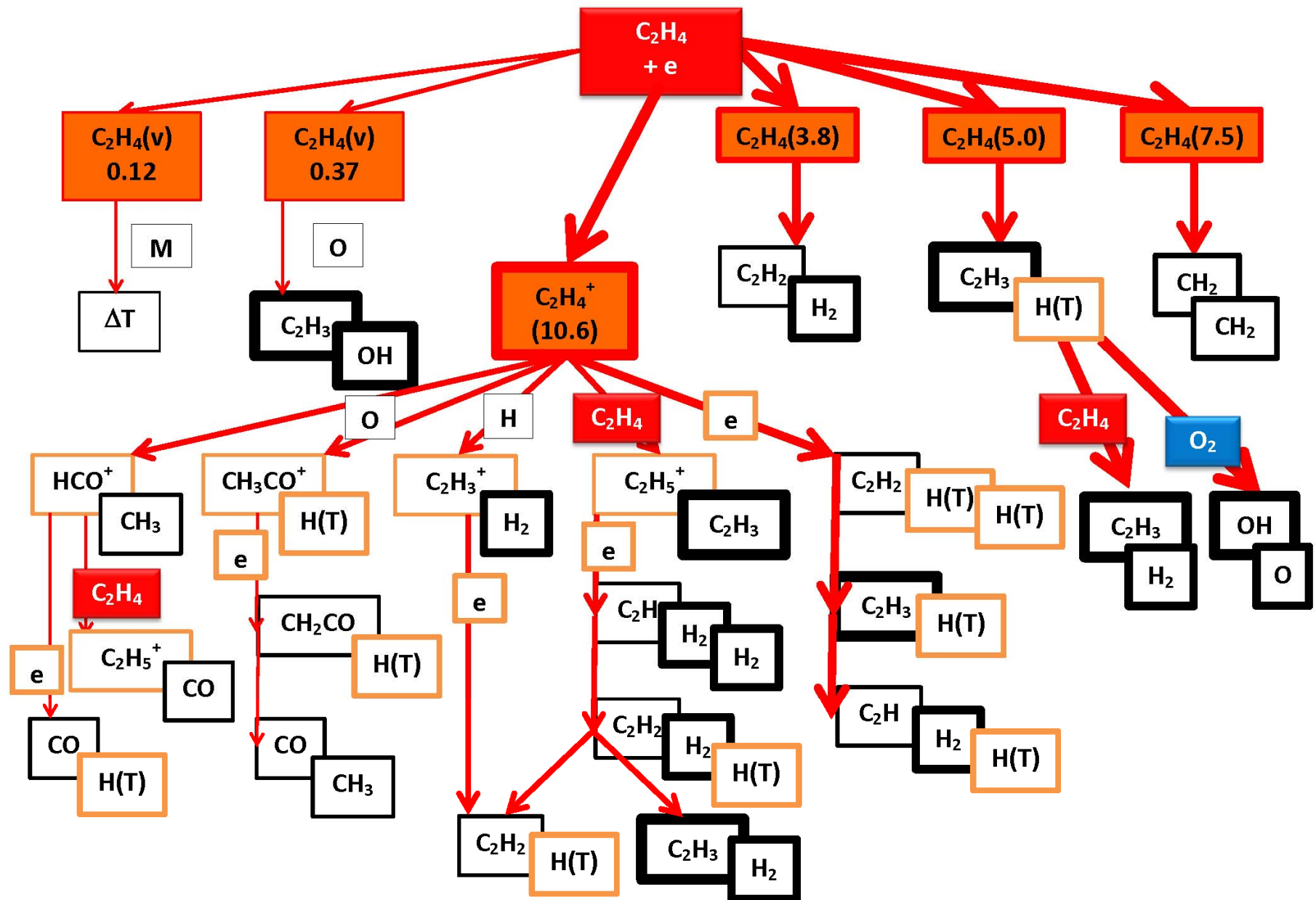


# Cross-sections Available

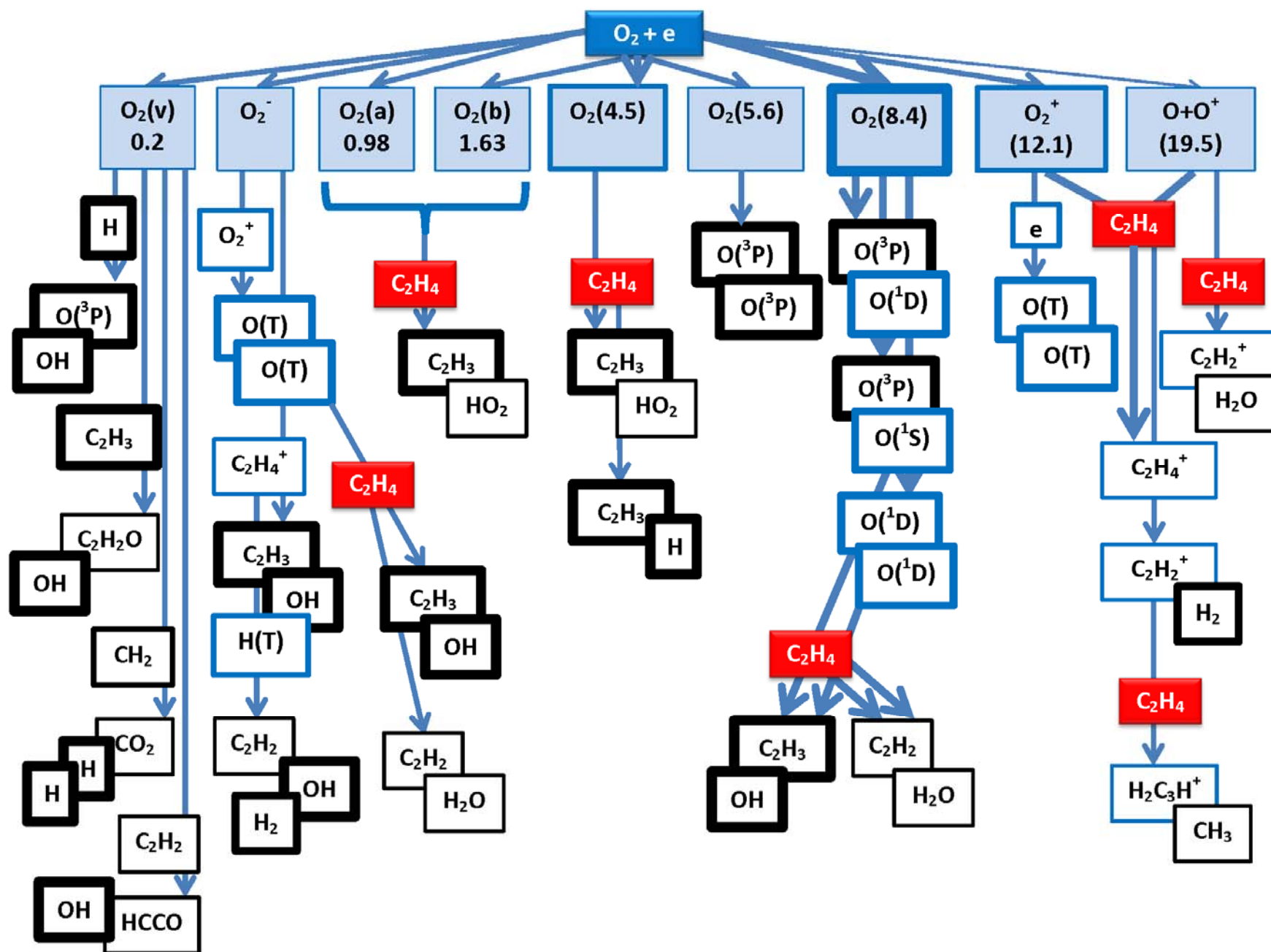
Atmospheric	Saturated	Unsaturated	Oxygenated	Isomers
N <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	CO	iso-butane
O <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	CH <sub>3</sub> OH	iso-propane
CO <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>5</sub> OH	neo-pentane
H <sub>2</sub> O	C <sub>4</sub> H <sub>10</sub>		CH <sub>3</sub> OCH <sub>3</sub> DME	
O <sub>3</sub>	C <sub>5</sub> H <sub>12</sub>			
Ar	H <sub>2</sub>			
N <sub>2</sub> O				



# PAC Pathways: C<sub>2</sub>H<sub>4</sub>-air

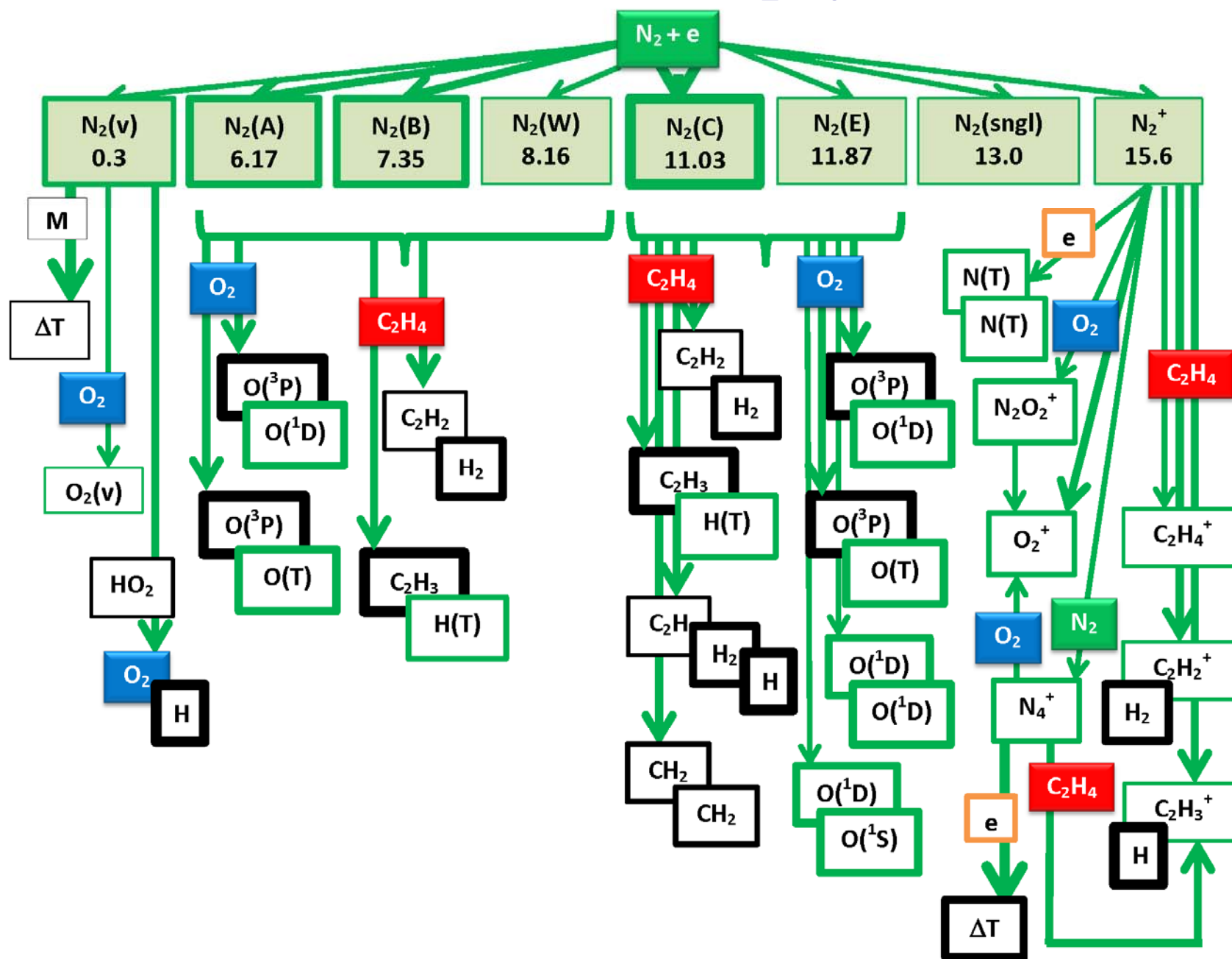


# PAC Pathways: C<sub>2</sub>H<sub>4</sub>-air



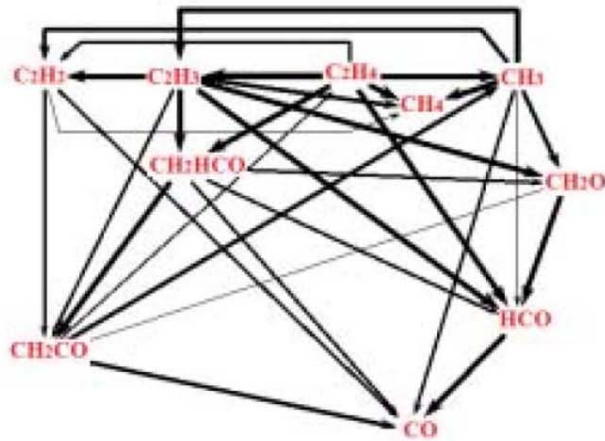


# PAC Pathways: C<sub>2</sub>H<sub>4</sub>-air

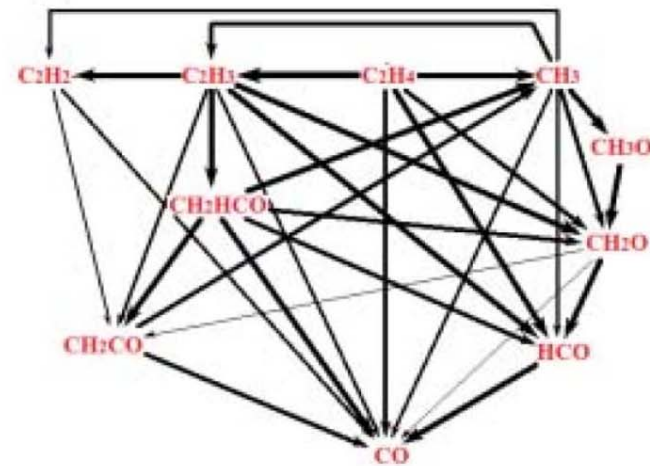




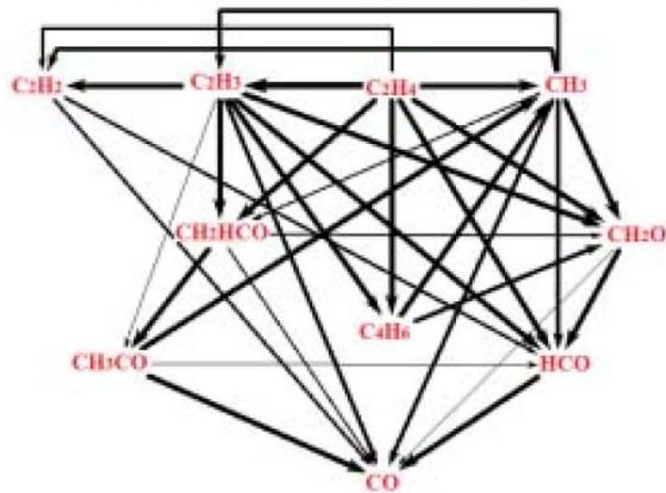
Pathway analysis in ignition process at the time of  $T=1360\text{K}$   
for  $\Phi = 1$ ,  $\text{Ar}=92\%$ ,  $P=2.1\text{atm}$  and initial  $T=1350\text{K}$ . Konnov, 2014



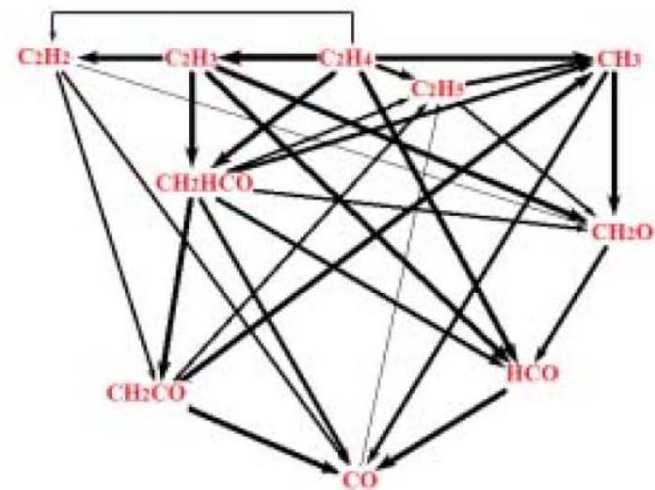
(LLNL nButane mechanism)



(USC mechanism)

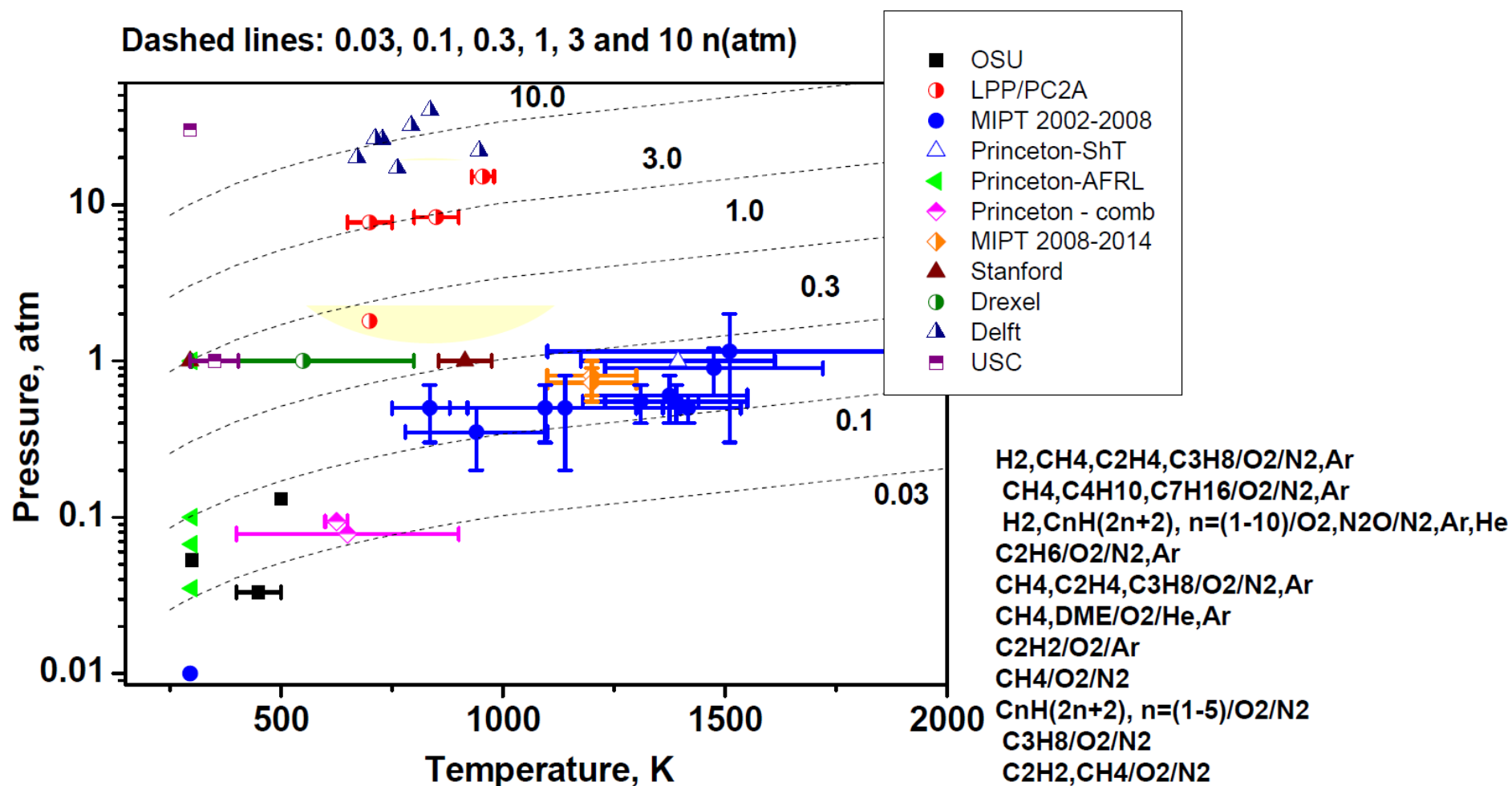


(Konnov mechanism)



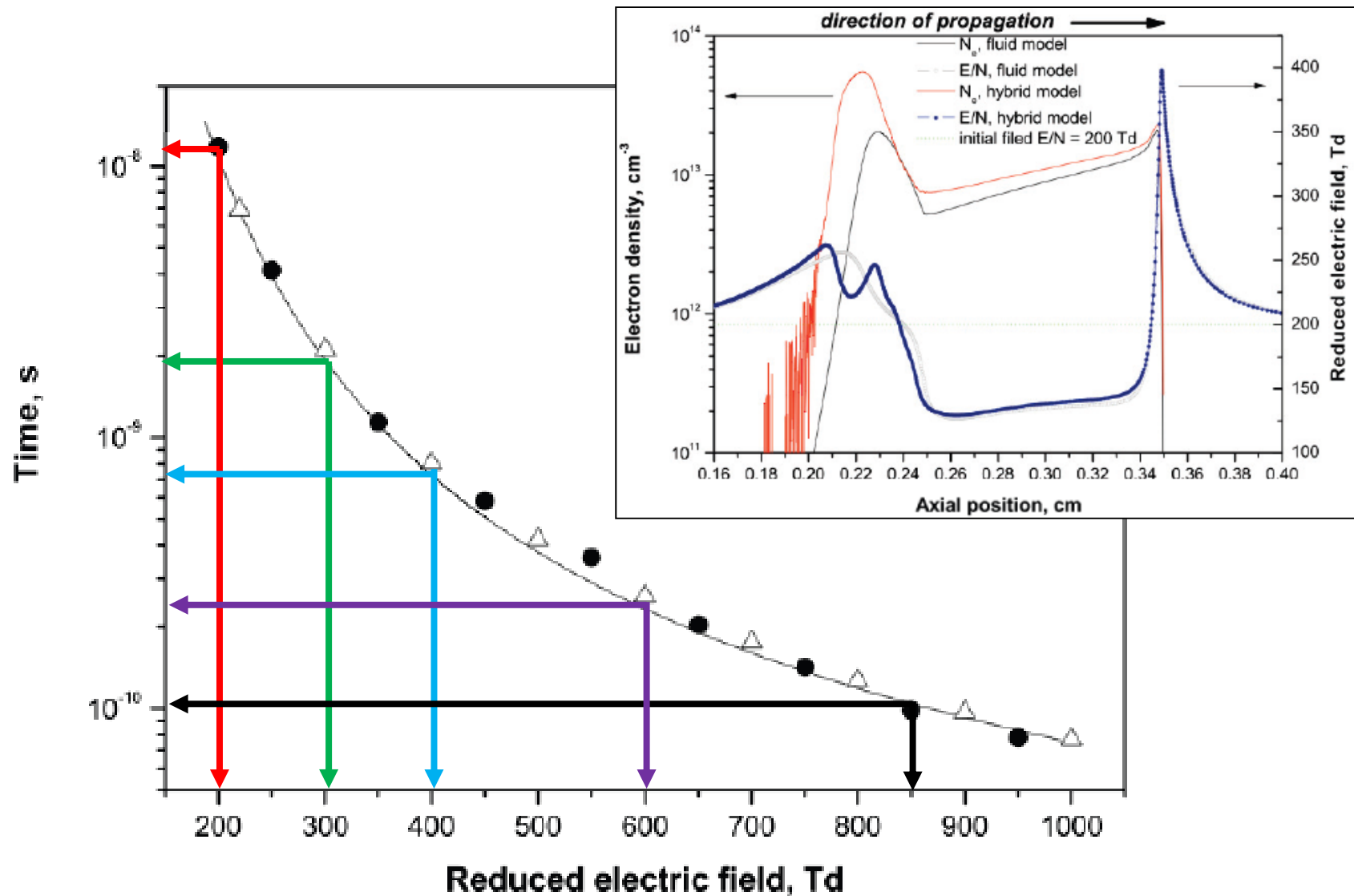
(UCSD mechanism)

# Where PAC Experimental Data is Available



S M Starikovskaia, J. Phys. D.: Appl. Phys, 47 (2014) 353001(34pp)

# Avalanche to Streamer Transition in Uniform Electric Field (air, 1 bar, 300 K, 1 cm, various $E/n$ )

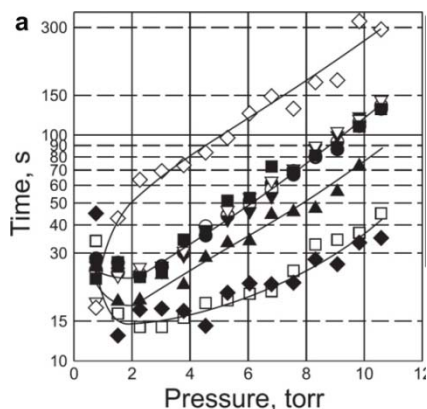


# Princeton Plasma Combustion Kinetics

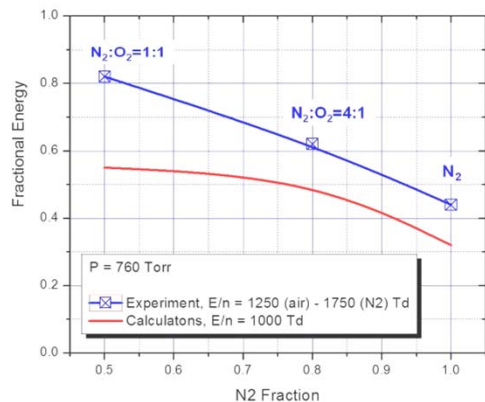
## Mechanism Validation

T = 300 K

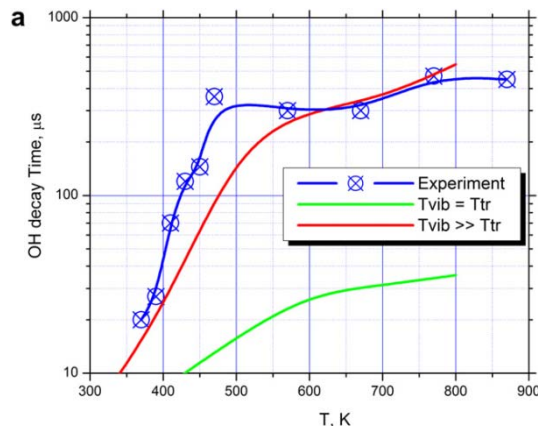
Slow Oxidation of H<sub>2</sub>, C1-C10  
P = 1-10 Torr



Fast Gas Heating Mechanism.  
N<sub>2</sub>-O<sub>2</sub> mixtures P = 0.2 – 1 atm



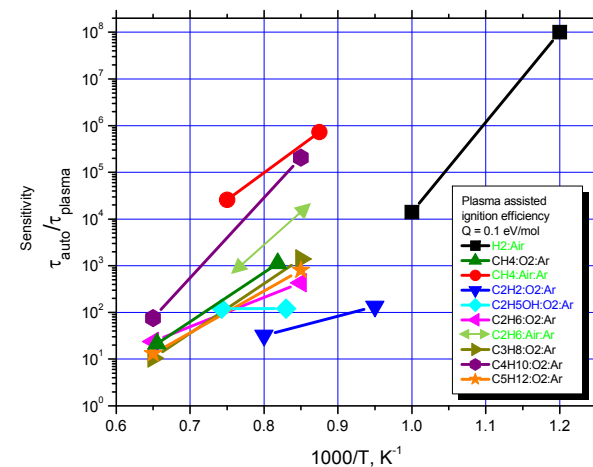
T = 300 - 800 K



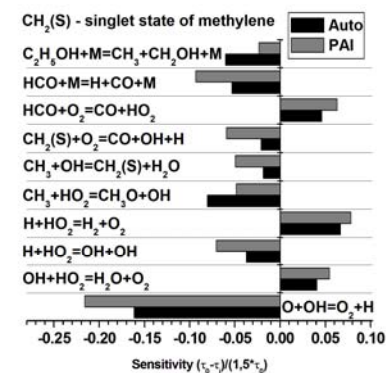
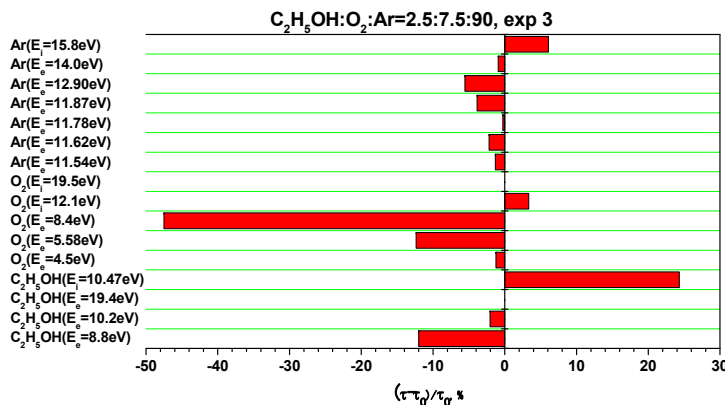
Oxidation Chains Development  
in Lean H<sub>2</sub>, CO, C1-C4 - Air  
Mixtures. P = 1 atm

T = 800 – 1700 K

Ignition Delay Time Reduction.  
H<sub>2</sub>, C1-C5, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OH – O<sub>2</sub>-Ar  
Mixtures. P = 0.3-0.5 atm



Sensitivity Analysis for Discharge and Combustion Stages



# SDBD Discharge and Fast Heating

Gate = 0.5 ns

Time shift between frames is 1 ns

The movie duration is 41 ns

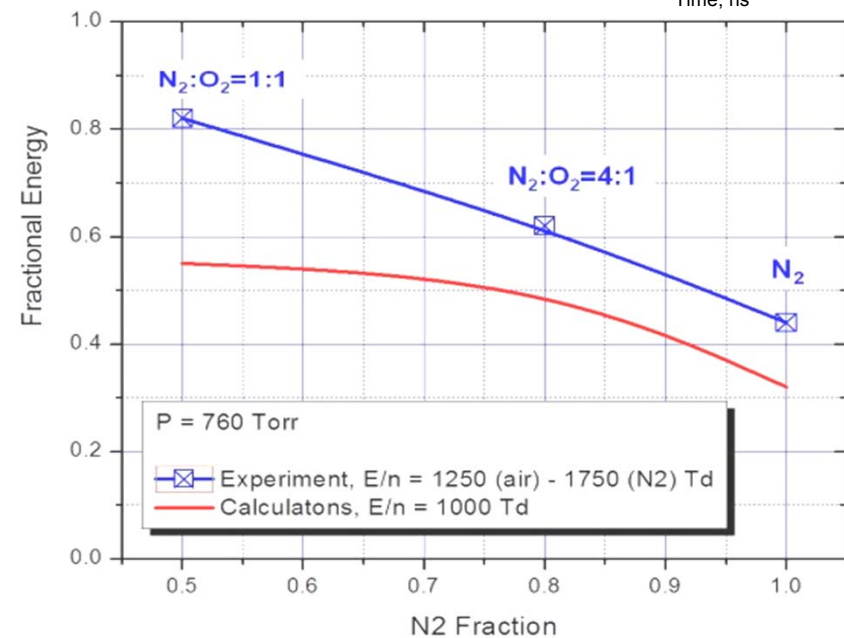
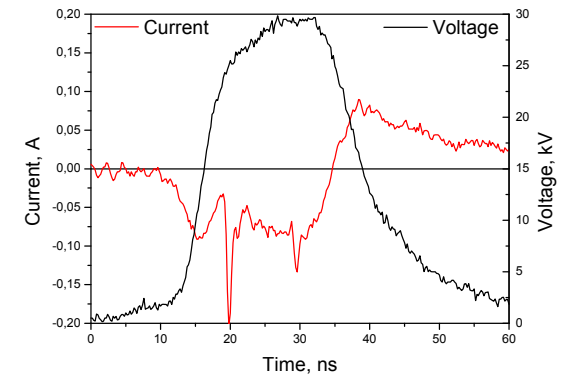
Impulse Parameters

$V = 14$  kV

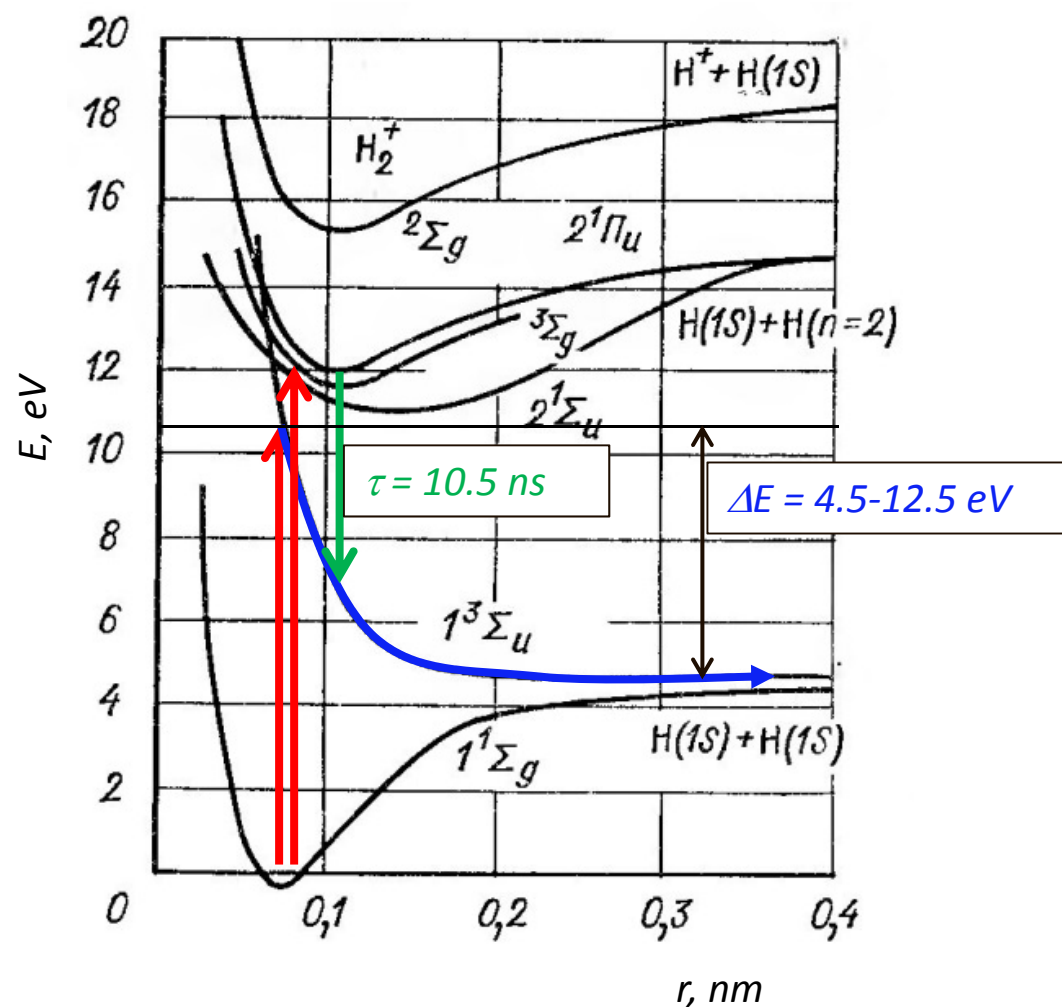
$t_{1/2} = 20$  ns

Frequency = 1 kHz

Velocity = 0.4 mm/ns



# Potential Energy Curves of Molecular Hydrogen

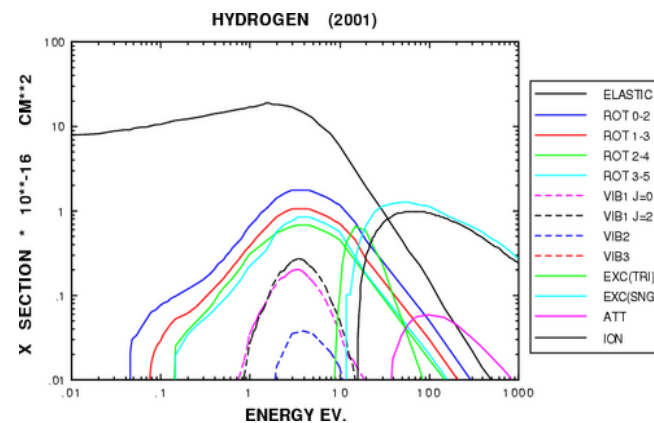


$H_2(b^3\Sigma_u)$ , 8.9 eV  
 $\sigma_{\max} = 0.33 \text{ \AA}^2 (17 \text{ eV})$

$H_2(a^3\Sigma_g)$ , 11.8 eV  
 $\sigma_{\max} = 0.12 \text{ \AA}^2 (15 \text{ eV})$

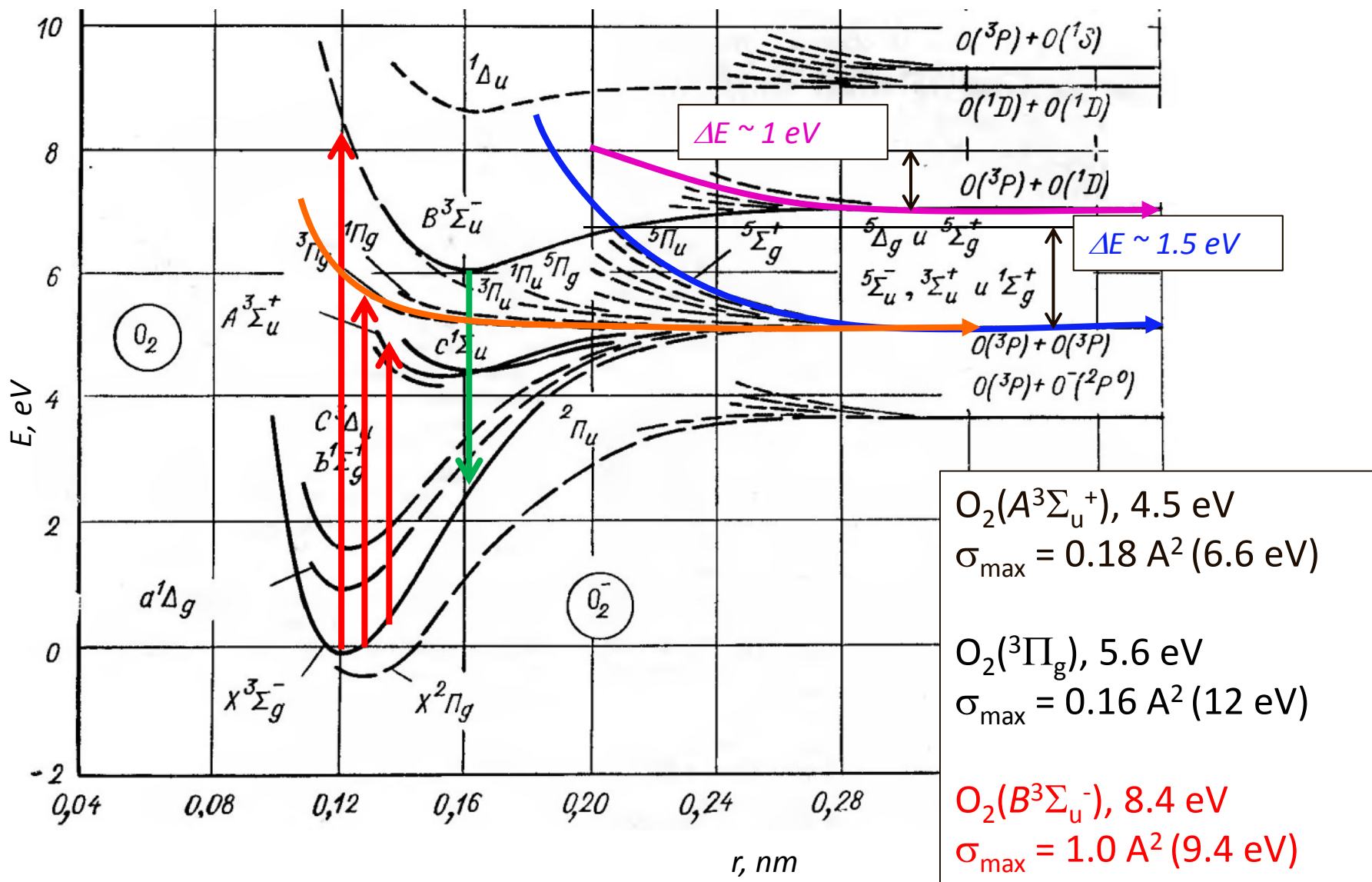
$H_2(B^1\Sigma_u)$ , 11.3 eV  
 $\sigma_{\max} = 0.48 \text{ \AA}^2 (40 \text{ eV})$

$H_2(C^1\Pi_u)$ , 12.4 eV  
 $\sigma_{\max} = 0.40 \text{ \AA}^2 (40 \text{ eV})$



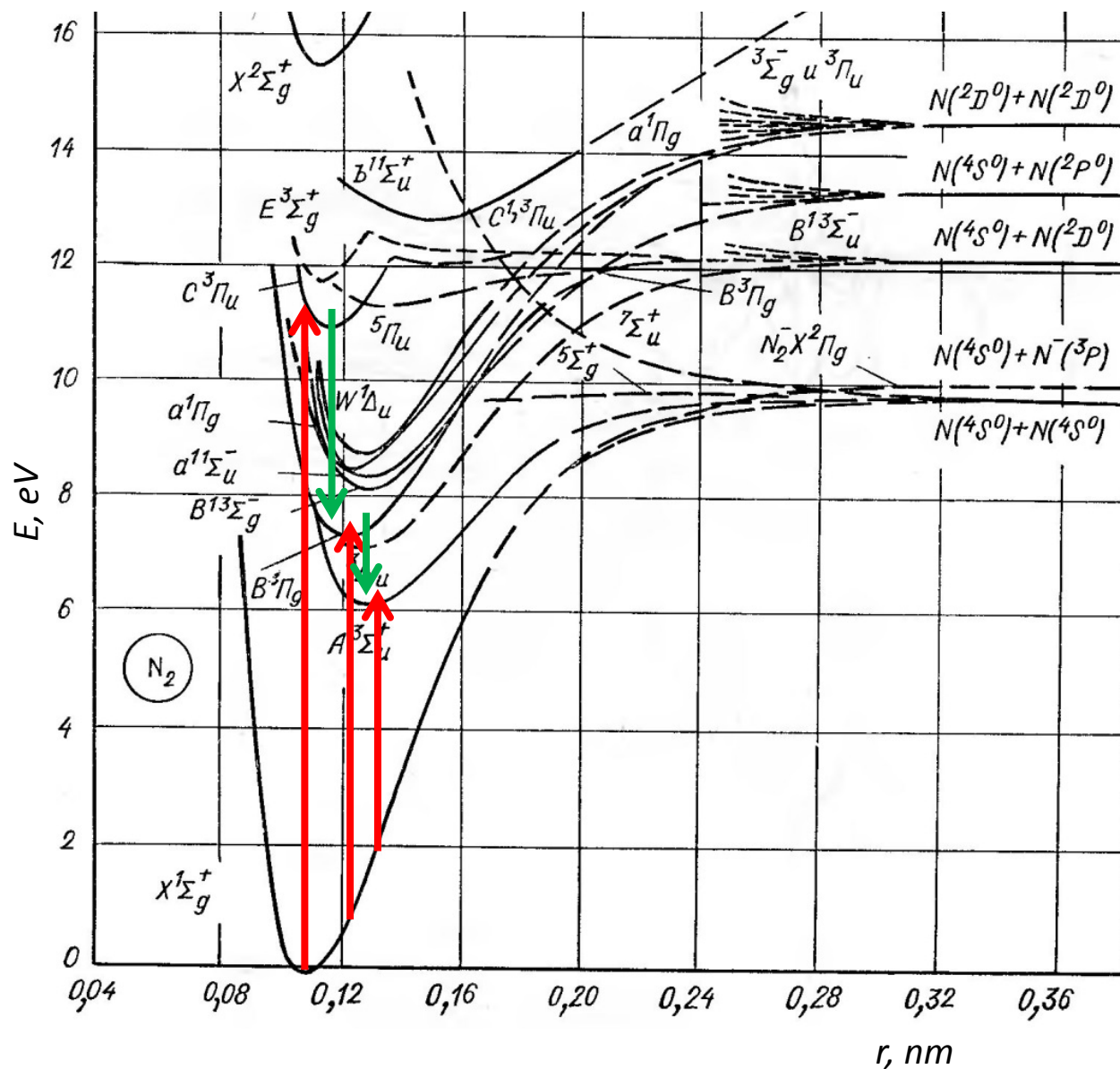


# Potential Energy Curves of Molecular Oxygen





# Potential Energy Curves of Molecular Nitrogen

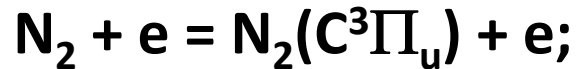


$N_2(A^3\Sigma_u^+)$ , 6.2 eV  
 $\sigma_{\max} = 0.08 \text{ \AA}^2 (10 \text{ eV})$

$N_2(B^3\Pi_g)$ , 7.35 eV  
 $\sigma_{\max} = 0.20 \text{ \AA}^2 (12 \text{ eV})$

$N_2(C^3\Pi_u)$ , 11.03 eV  
 $\sigma_{\max} = 0.98 \text{ \AA}^2 (14 \text{ eV})$

# Major Channels of Hot Atoms Production



$$k = f(E/n)$$

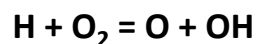


$$k = f(E/n)$$



$$k = f(E/n)$$

# Chain Initiation/Branching Reactions



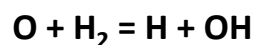
$$k = 1.6 \times 10^{-10} \times \exp(-7470/T) \text{ cm}^3/\text{s}$$

$$k(300) = 2.5 \times 10^{-21} \text{ cm}^3/\text{s}$$

$$k(\text{hot}) = 1.6 \times 10^{-10} \text{ cm}^3/\text{s}$$



$$k(300, 1 \text{ atm}) = 1.6 \times 10^{-12} \text{ cm}^3/\text{s} \quad T_{\text{crit}} \sim T_{\text{autoignition}}$$



$$k = 8.5 \times 10^{-20} \times T^{2.67} \times \exp(-3160/T) \text{ cm}^3/\text{s}$$

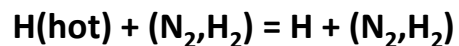
$$k(300) = 9.3 \times 10^{-18} \text{ cm}^3/\text{s}$$

$$k(\text{hot}) = 1.5 \times 10^{-10} \text{ cm}^3/\text{s}$$

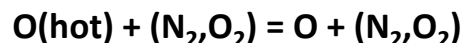
$$k(^1\text{D}) = 1.1 \times 10^{-10} \text{ cm}^3/\text{s}$$



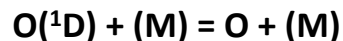
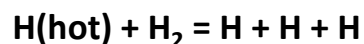
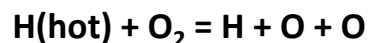
$$k(300, 1 \text{ atm}) = 2.2 \times 10^{-14} \text{ cm}^3/\text{s} \quad T_{\text{crit}} \sim 650\text{K}$$



$$k \sim 2m/M k_{\text{gk}} \sim 1.6 \times 10^{-10} \text{ cm}^3/\text{s}$$



$$k \sim 2m/M k_{\text{gk}} \sim 1.3 \times 10^{-10} \text{ cm}^3/\text{s}$$

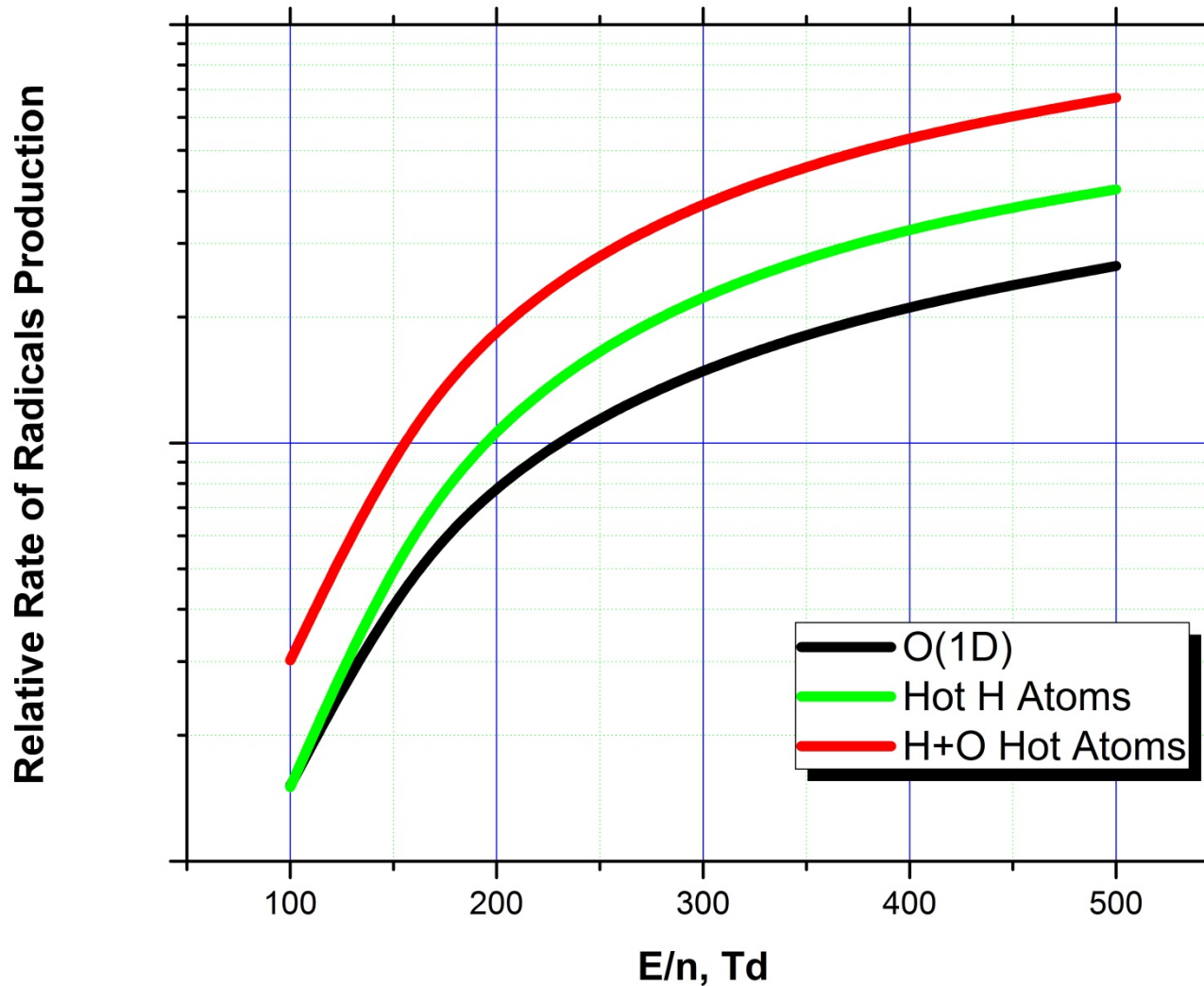


$$k = 2.6 \times 10^{-11} \text{ cm}^3/\text{s} \text{ (M} = \text{O}_2\text{)}$$

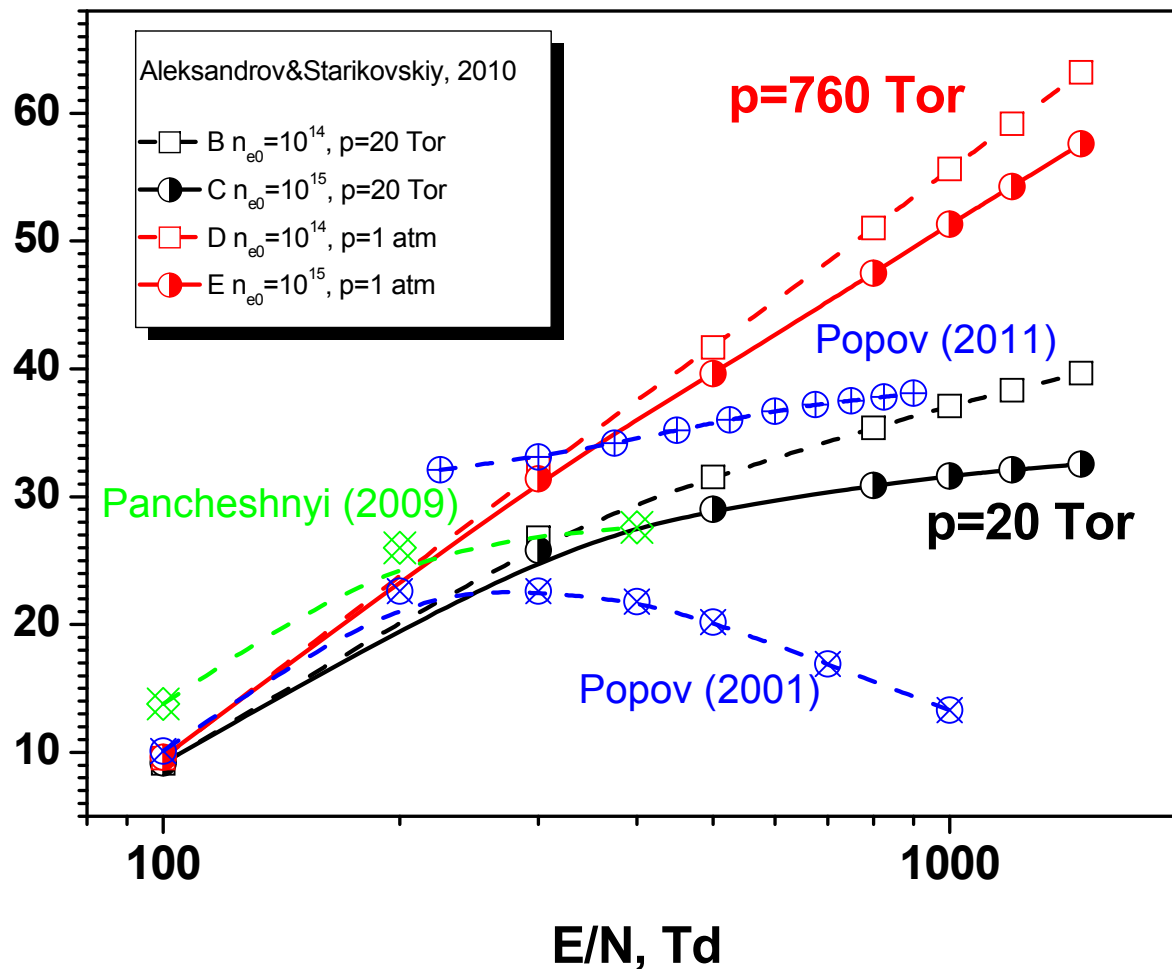
$$k = 1.3 \times 10^{-11} \text{ cm}^3/\text{s} \text{ (M} = \text{N}_2\text{)}$$

$$k = 5.2 \times 10^{-11} \text{ cm}^3/\text{s} \text{ (M} = \text{H}_2\text{)}$$

# Radicals Production Increase in Cold H<sub>2</sub>-Air Mixture Due to Hot Atoms Formation



# Mechanism of Fast Heating in Discharge Plasmas (high E/N)

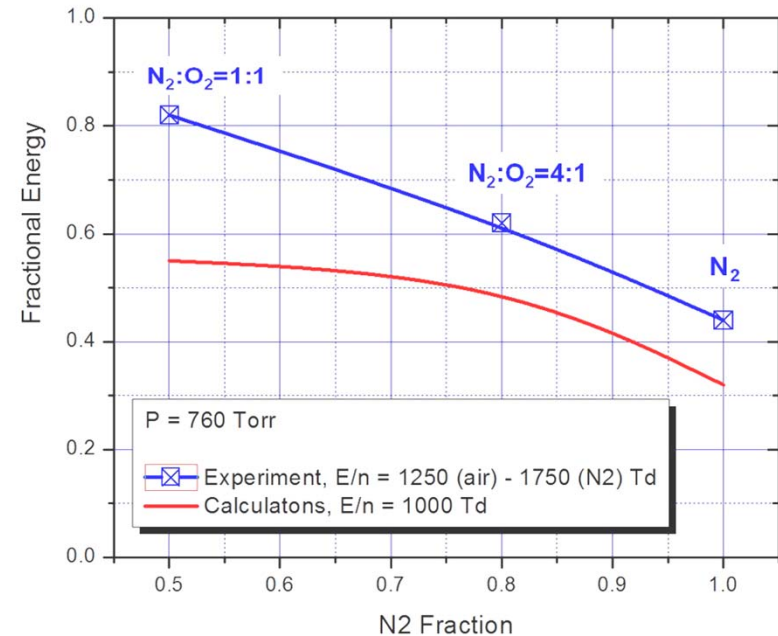
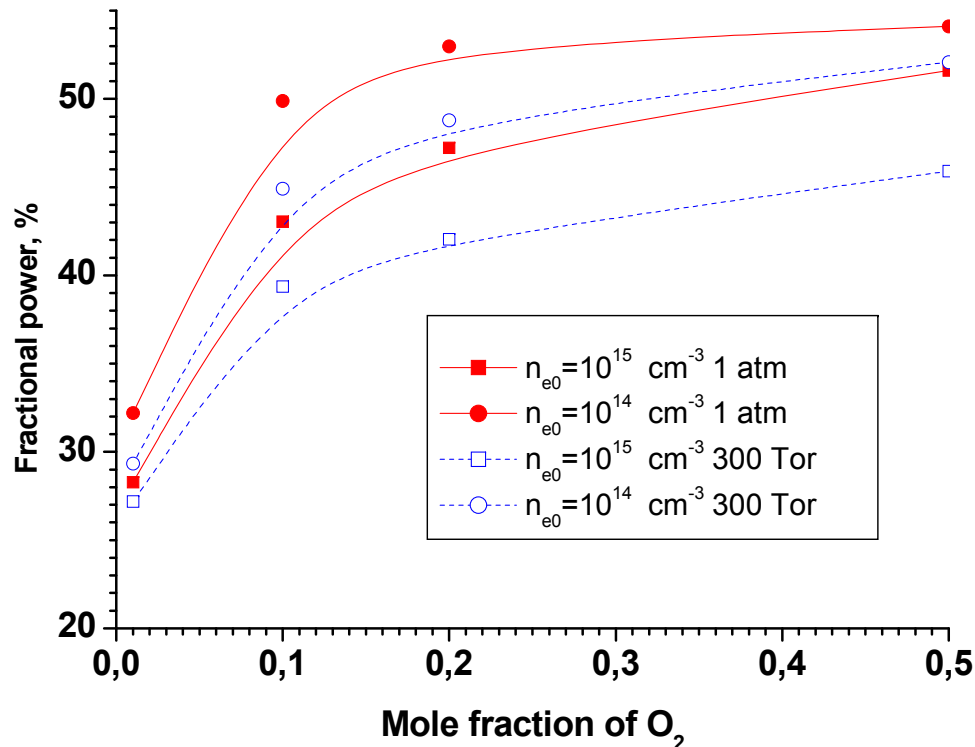


High (> 200 Td) E/N:

electron-ion and  
ion-ion  
recombination  
kinetics

# Fractional Electron Power Transferred Into Heat in N<sub>2</sub>:O<sub>2</sub> Mixtures

$$E/N = 10^3 \text{ Td}$$



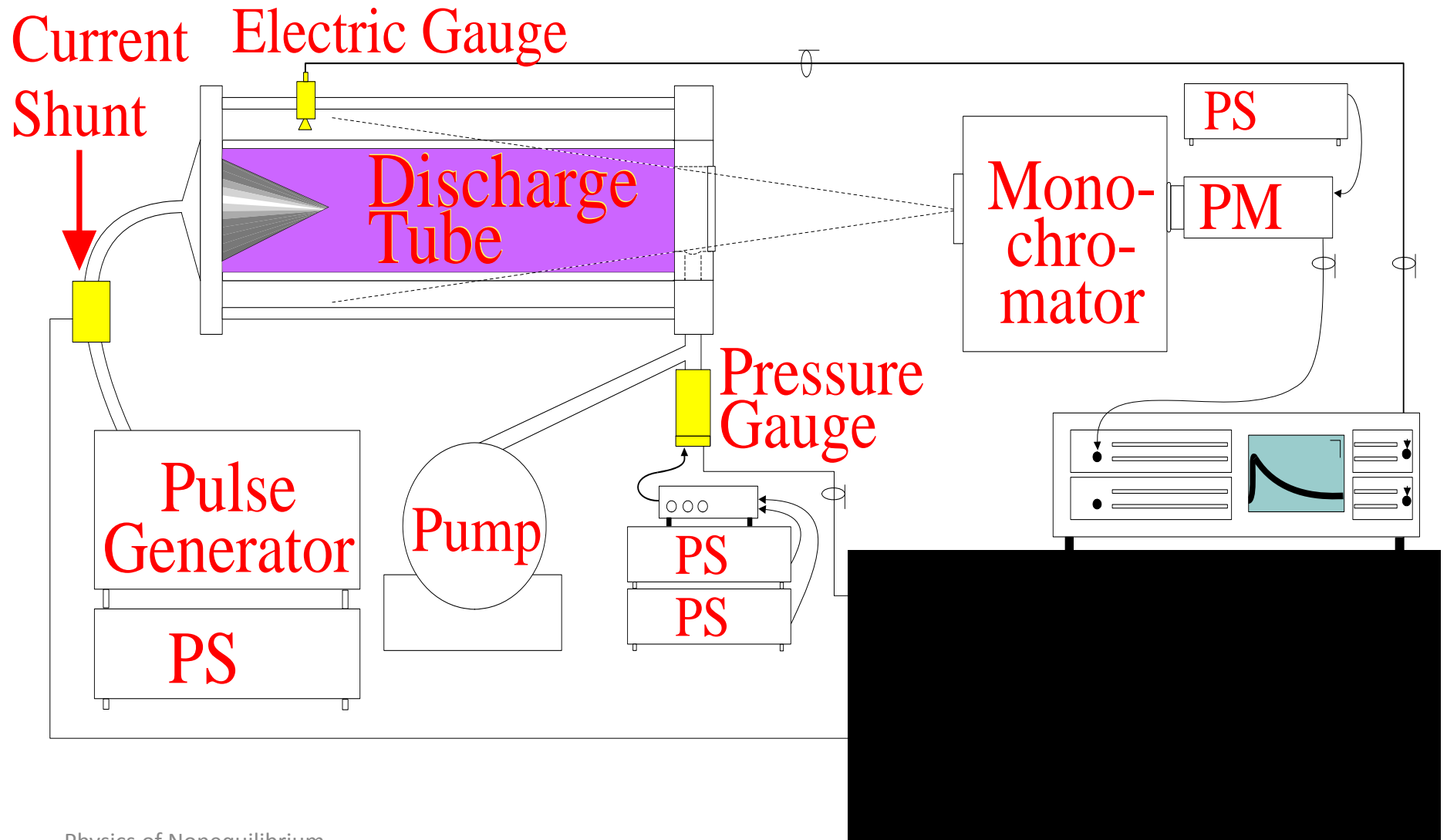
**Oxygen is required  
for efficient fast heating!**



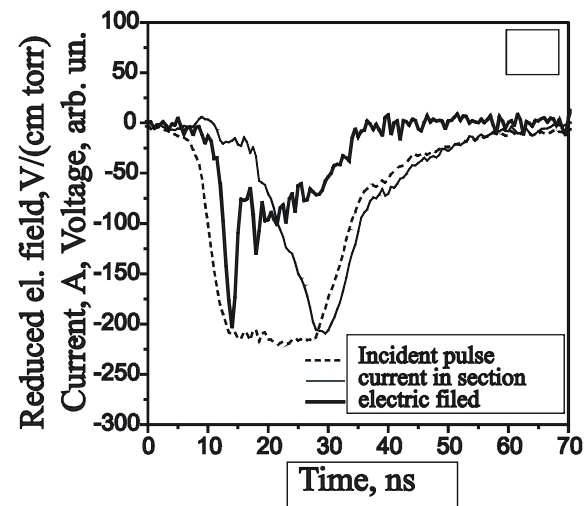
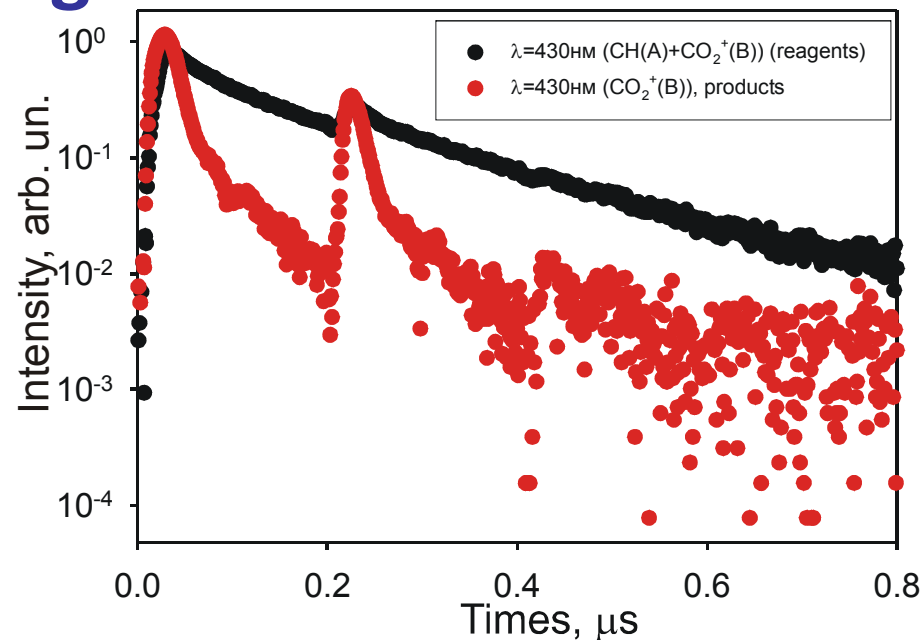
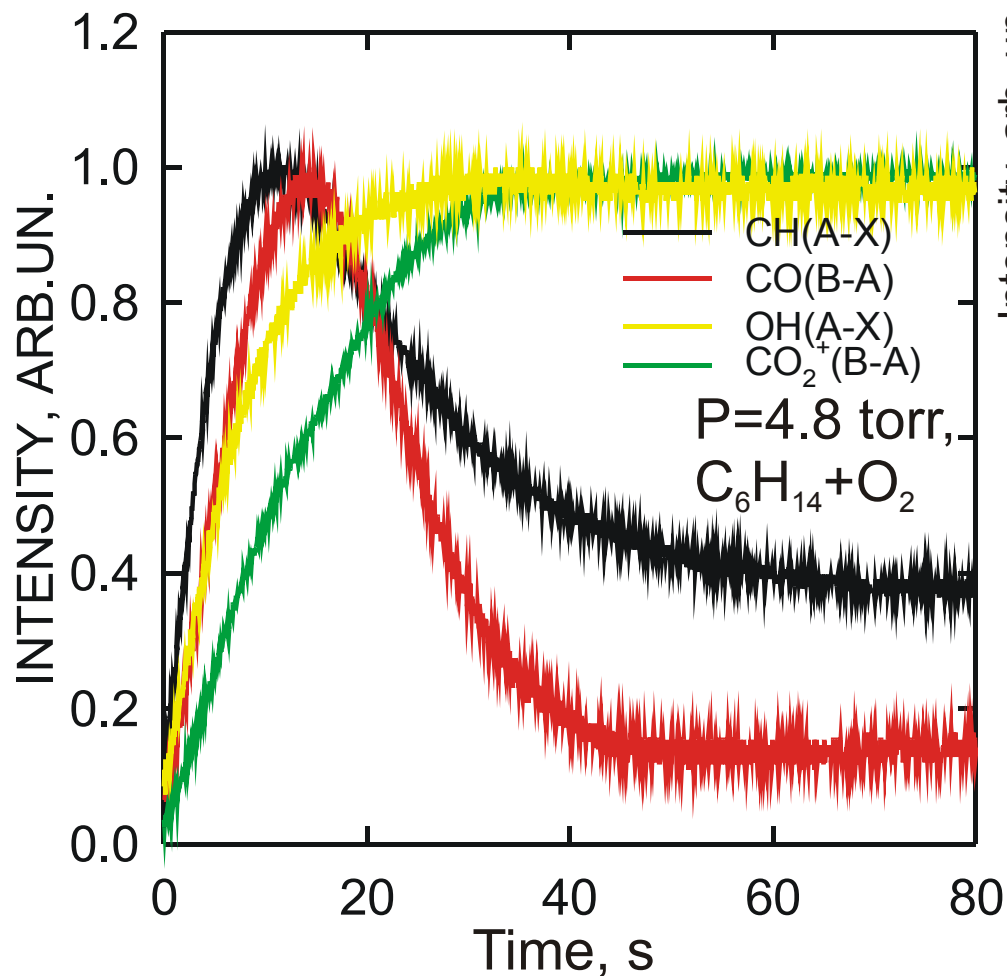
...



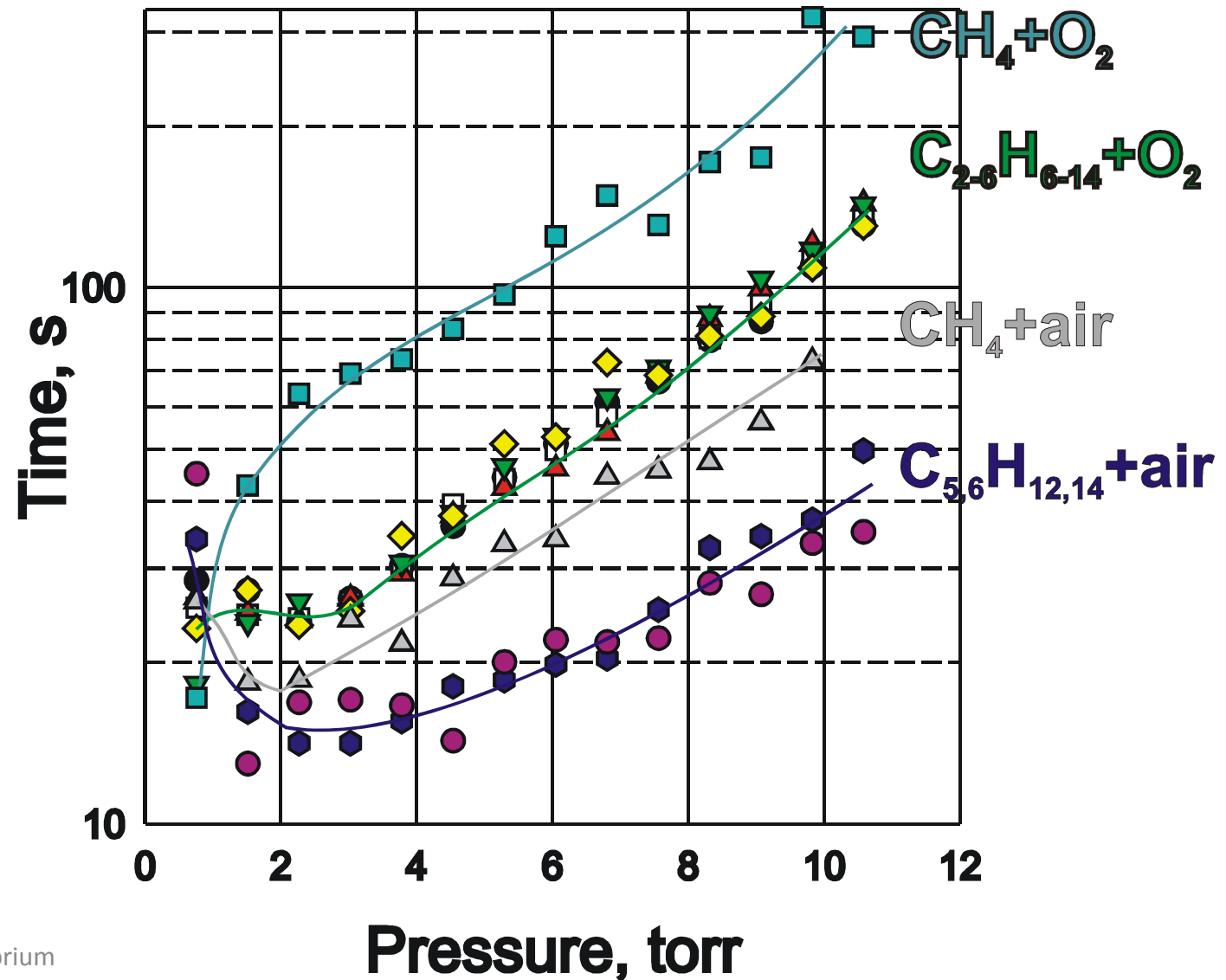
# Experimental Setup



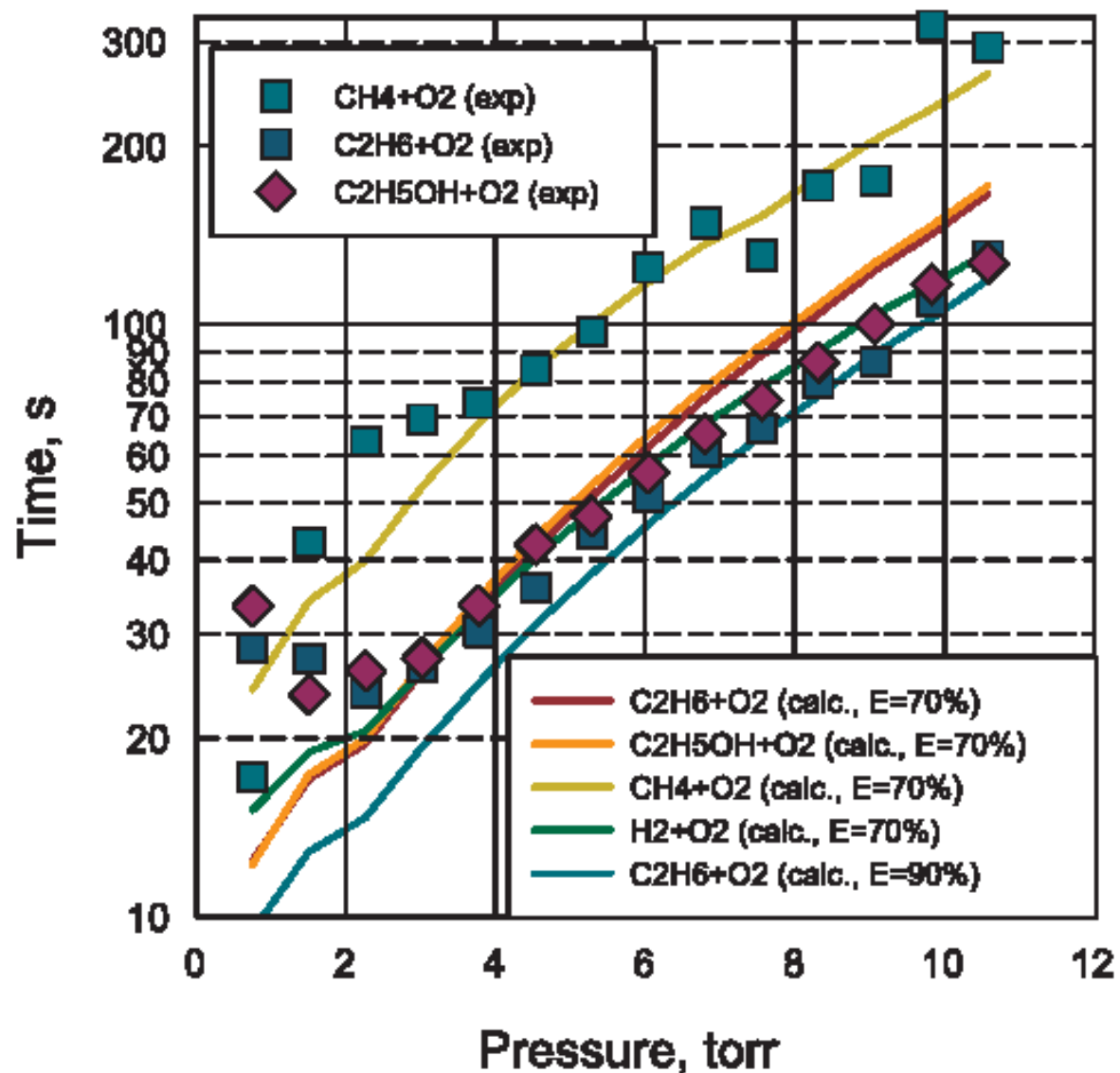
# Hexane Oxidation by Pulsed Nanosecond Discharge



# Hydrocarbon Oxidation Efficiency for $C_1$ - $C_6$ / $O_2$ / Air Mixtures

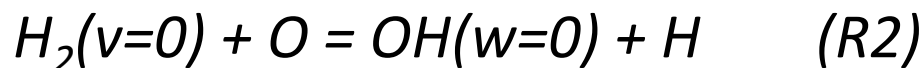
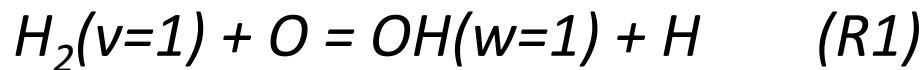
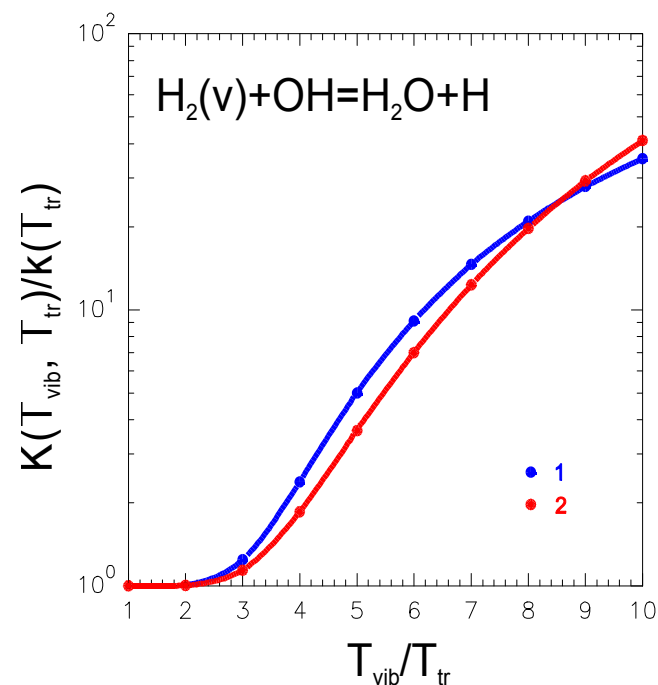
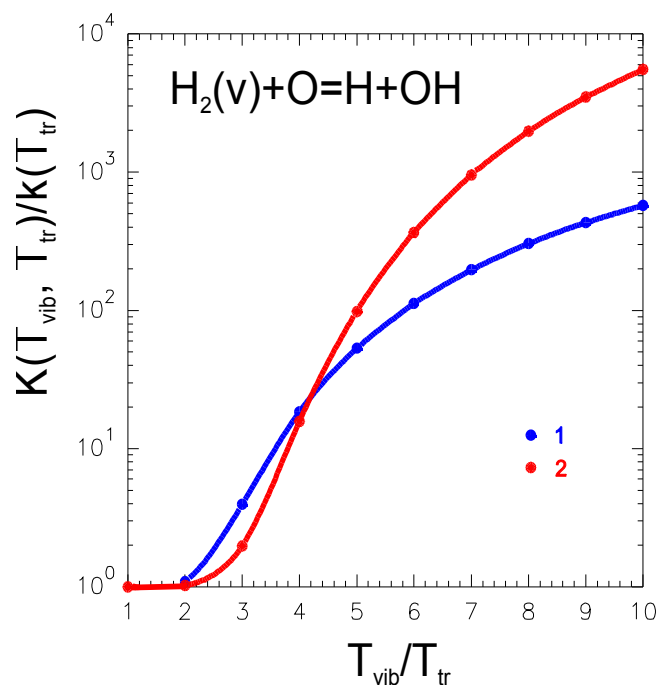


# Calculated and Measured Times of Oxidation



# Chemical Reactions with Excited Reagents

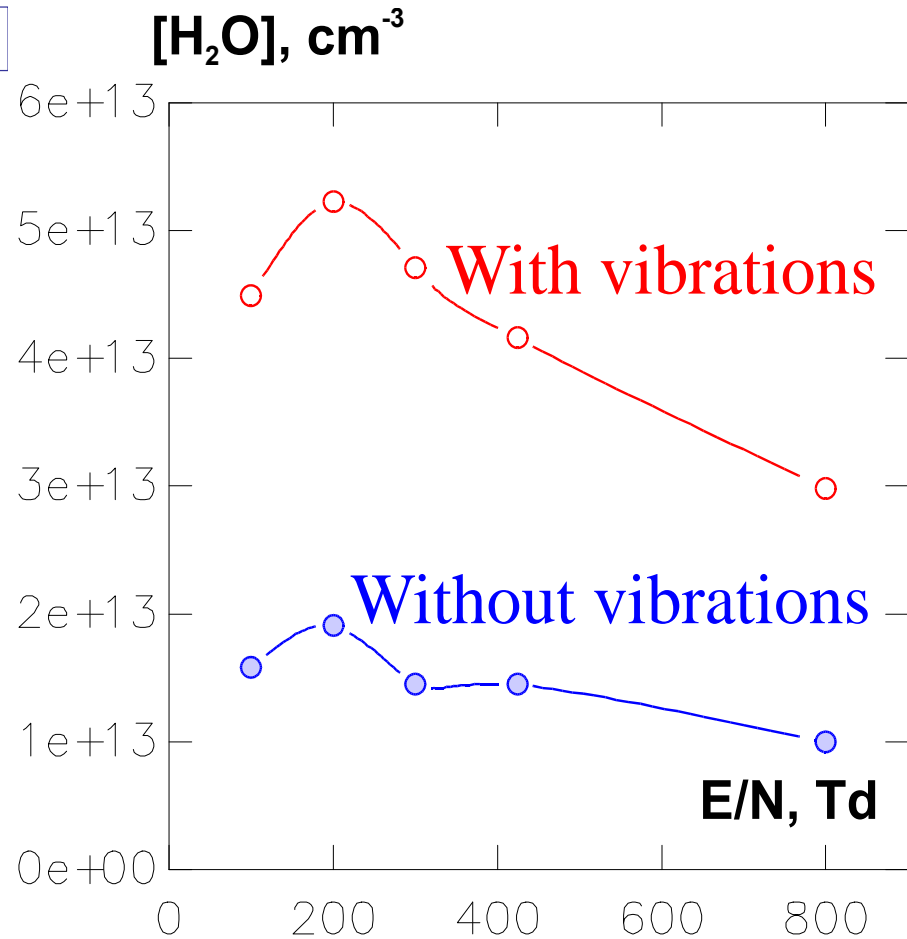
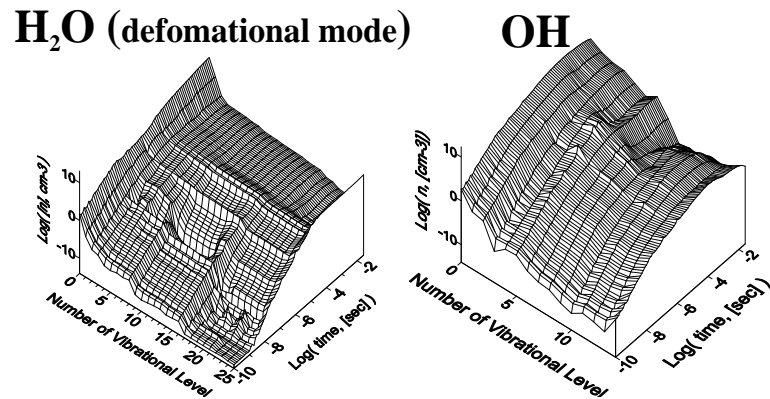
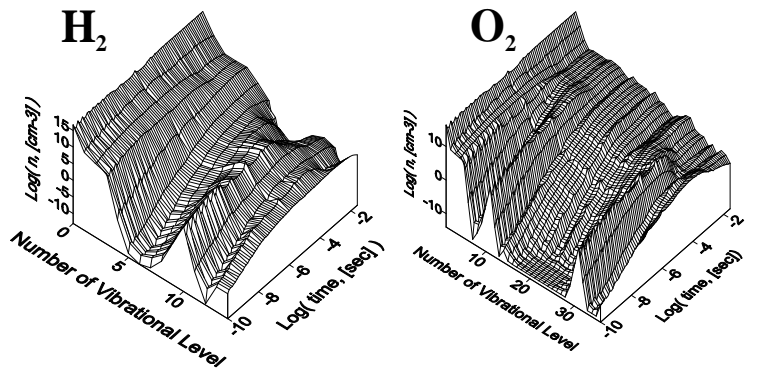
$AB(v)+C = A + BC(w)$   
Rate constant from  
modified  $\alpha$ -model  
(Starikovskii, Lashin 1996)



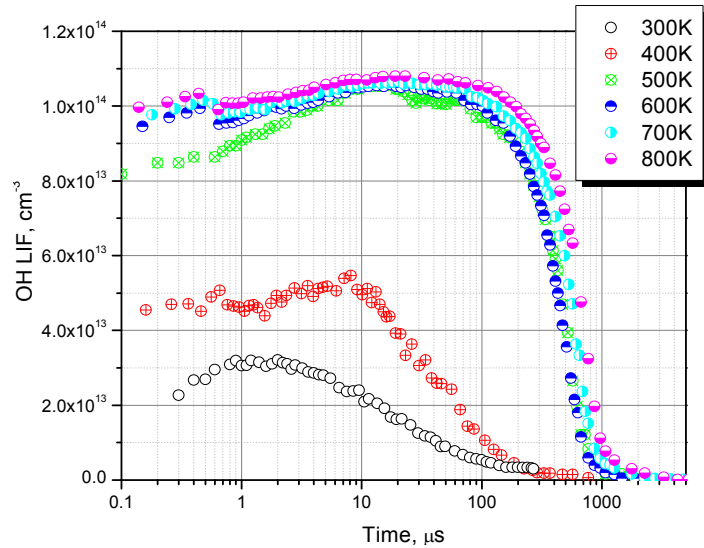
$$(k_{R1}/k_{R2})_{\text{exp}} = 2600 \text{ (O'Neal, Benson 1973); } (k_{R1}/k_{R2})_{\text{theor}} = 2750$$

# Kinetics. Influence of Vibrations

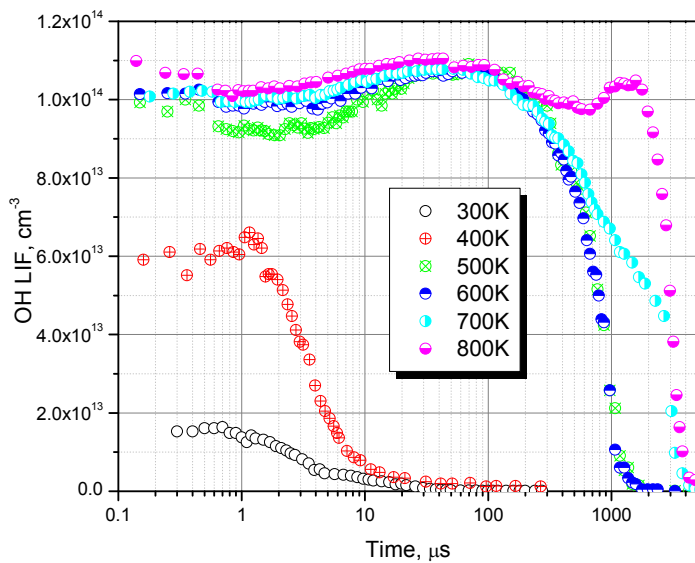
Distribution Of Vibrational-Excited Components



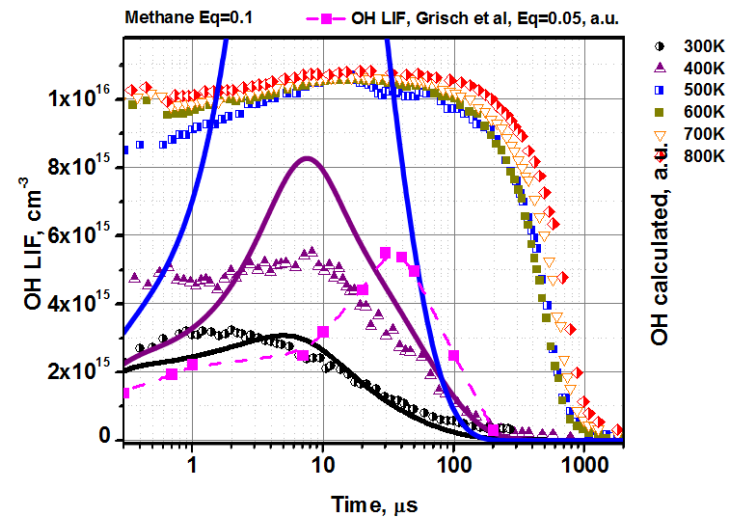
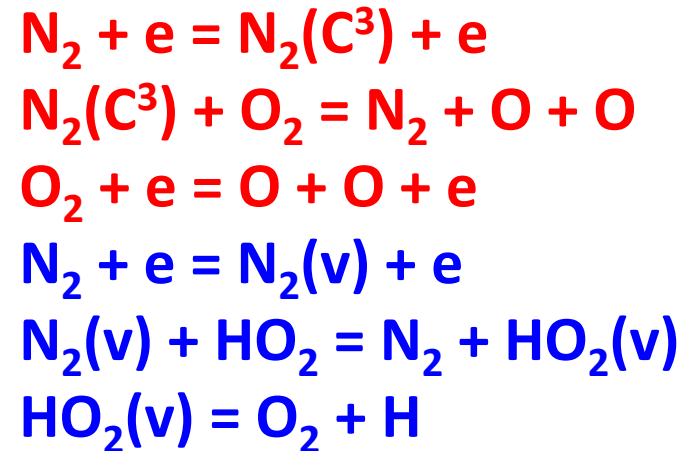
# Influence of Vibrational Excitation on Low-Temperature Kinetics



CH<sub>4</sub>-air



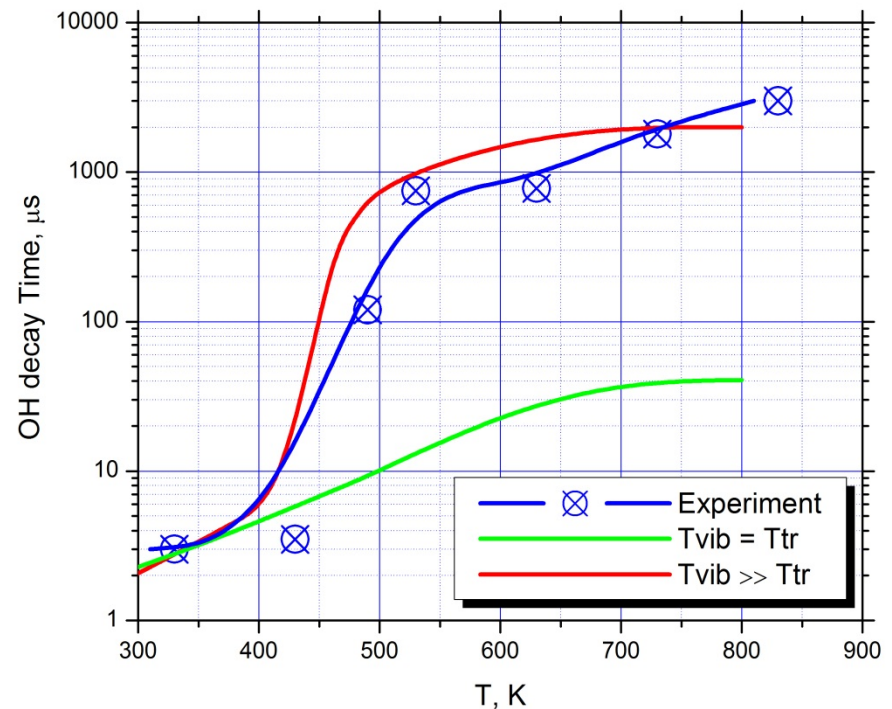
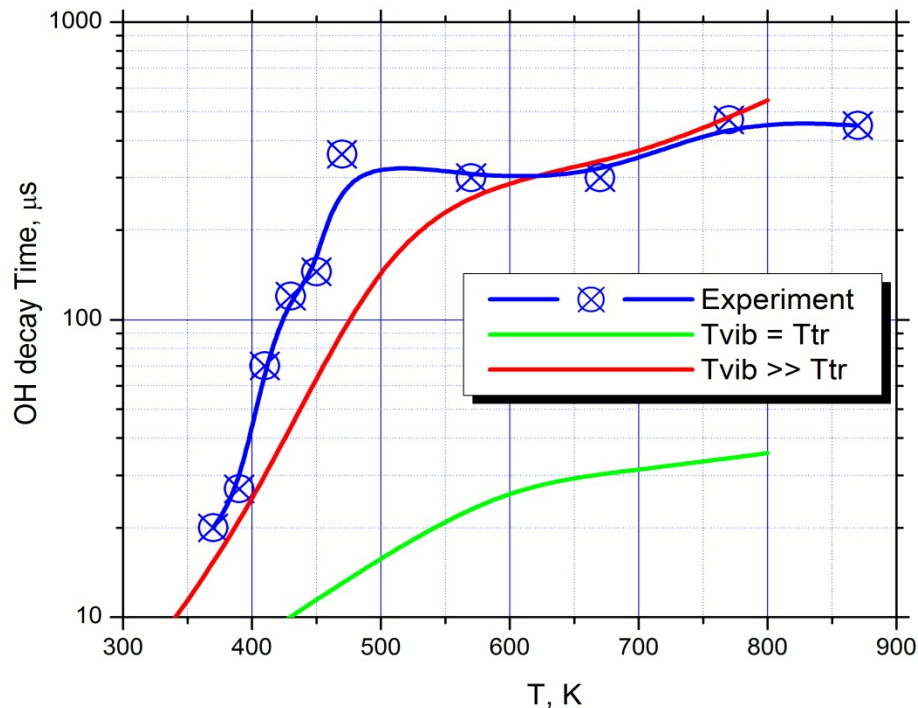
C<sub>4</sub>H<sub>10</sub>-air



Experiments: L Wu, J Lane, N P Cernansky, D L Miller, A A Fridman, A Yu Starikovskiy, *Proc. of Comb. Inst.*, 2010  
Modelling: D Levko, A I Schedrin, V V Naumov, S Starikovskaia, 2010



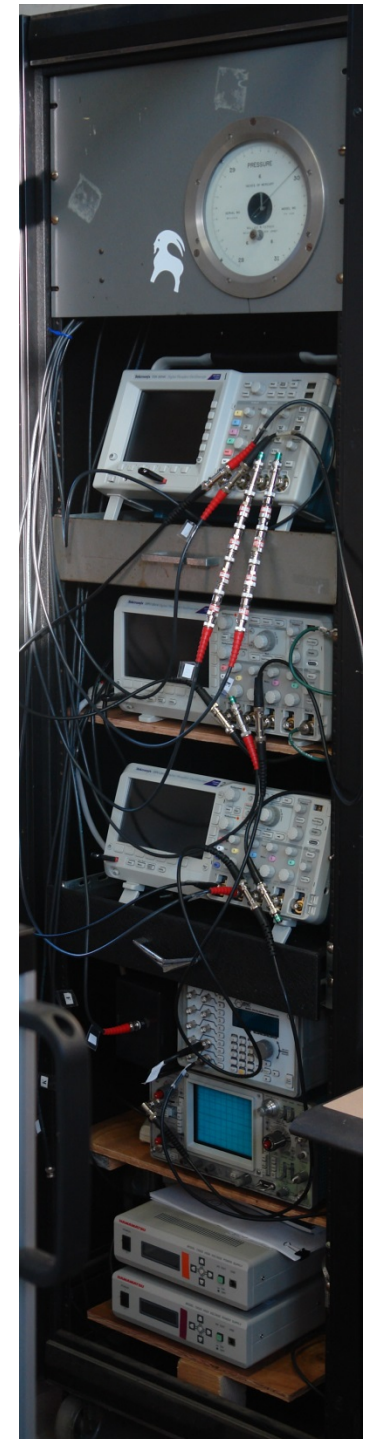
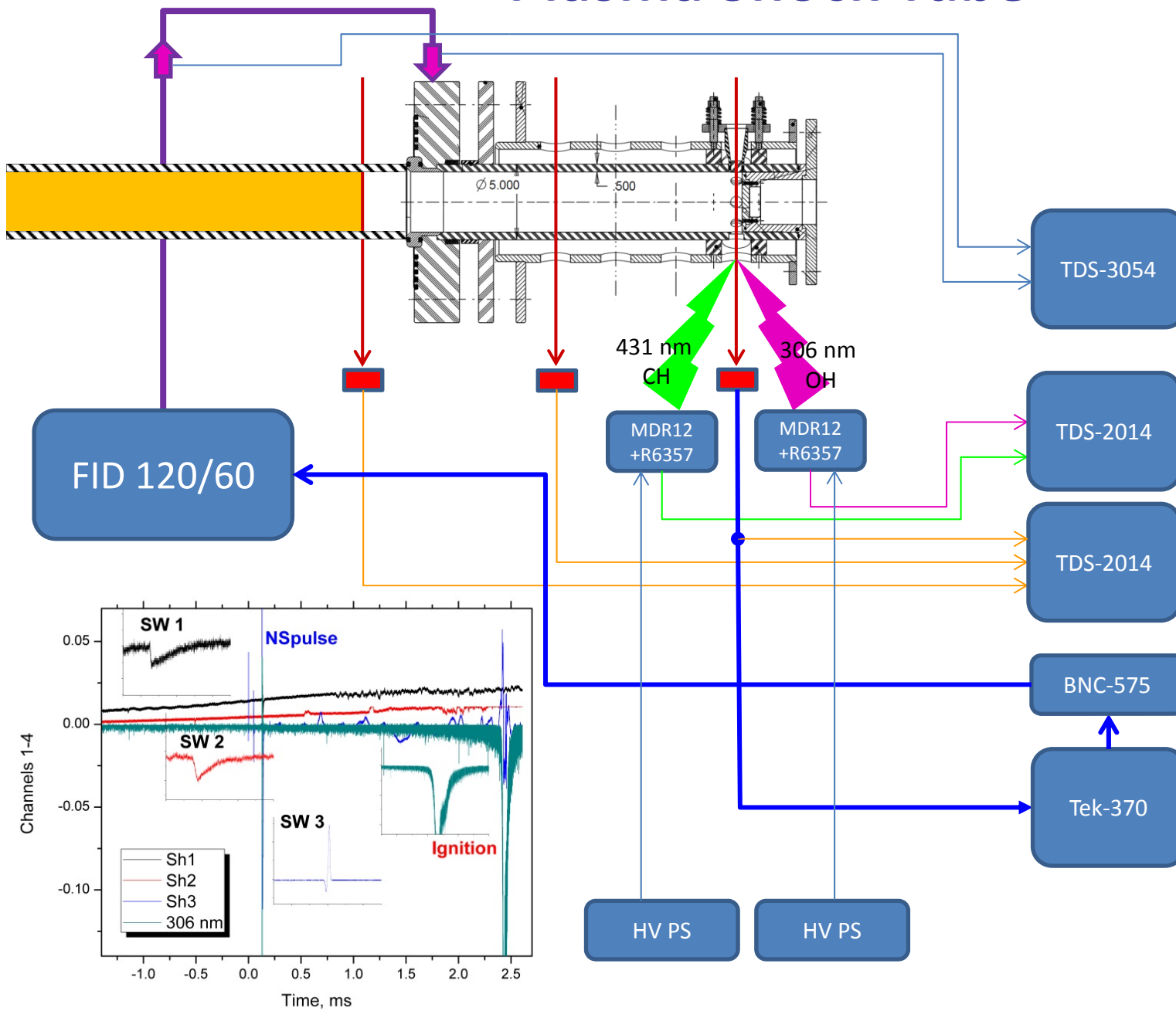
# Influence of Vibrational Excitation on Low-Temperature Kinetics: $\text{H}_2\text{O}_2$ Decomposition



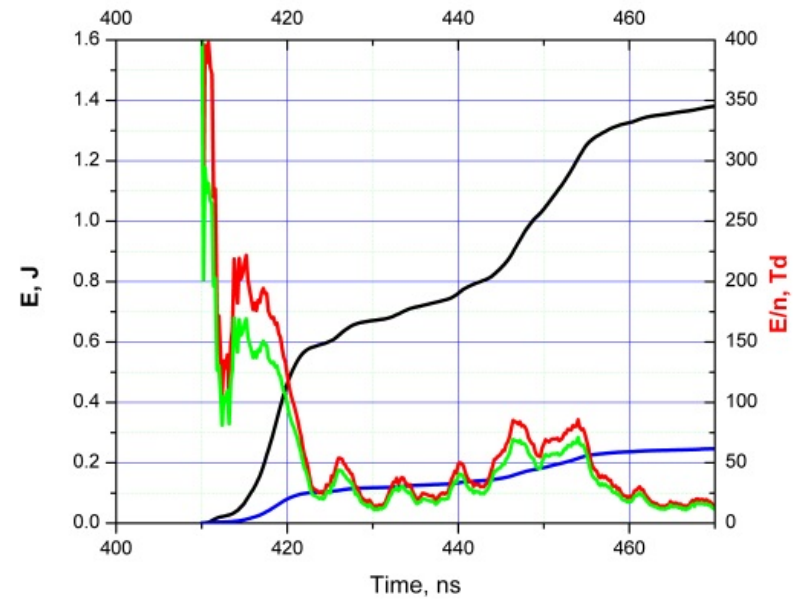
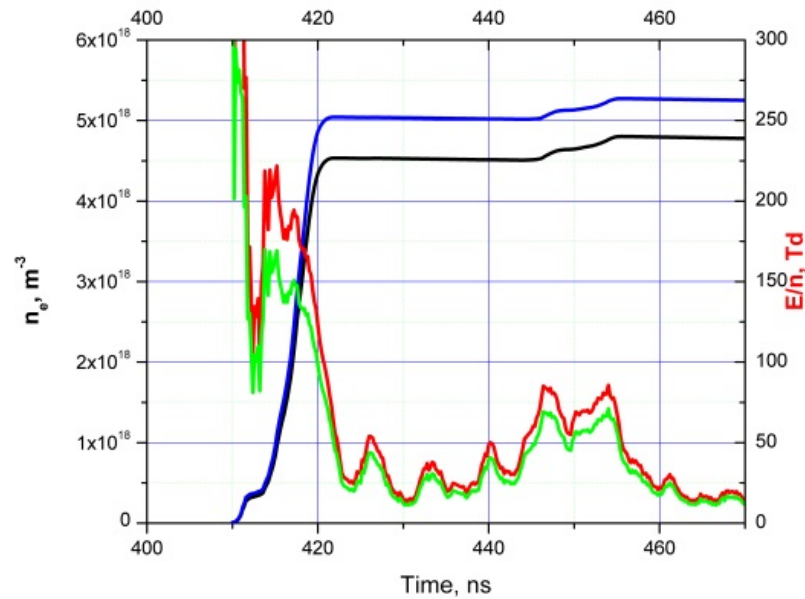
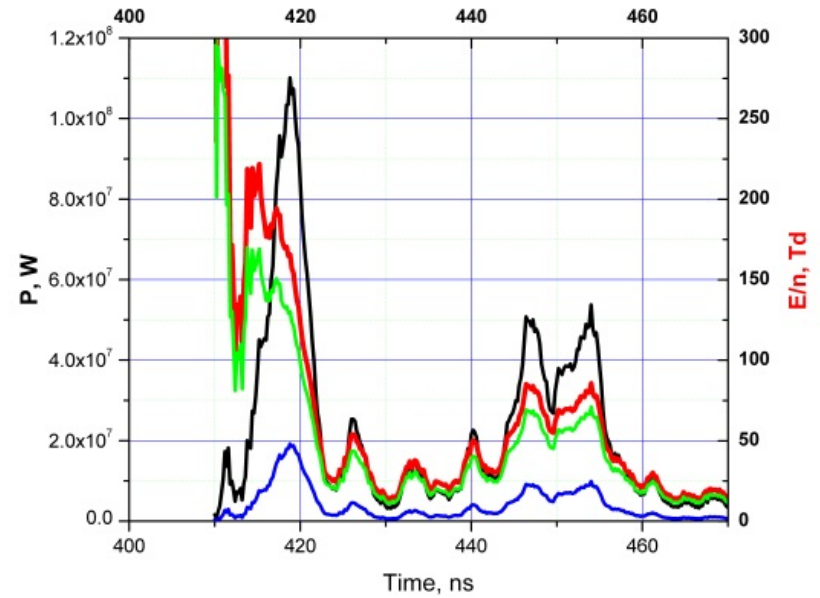
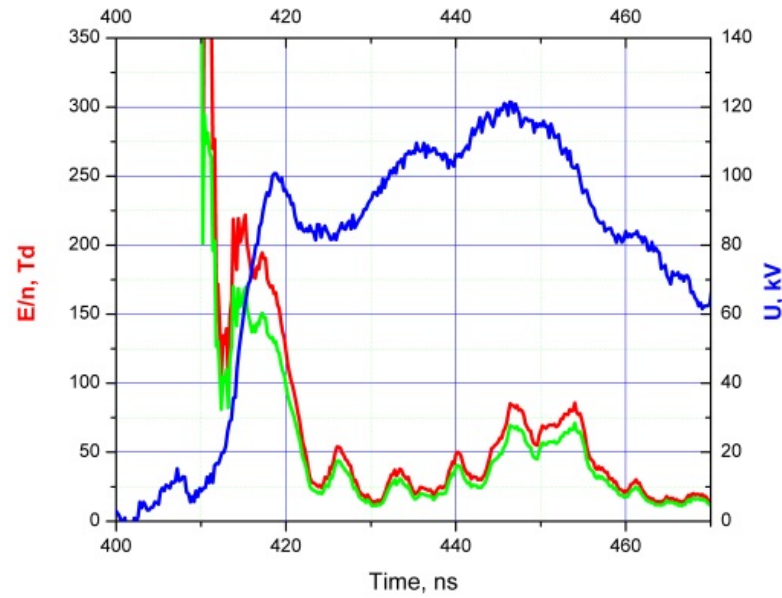
Measured and calculated OH decay time.  $P = 1$  atm.

a) 3% $\text{H}_2$  + air; b) 0.3% $\text{C}_4\text{H}_{10}$  + air.

# Plasma Shock Tube

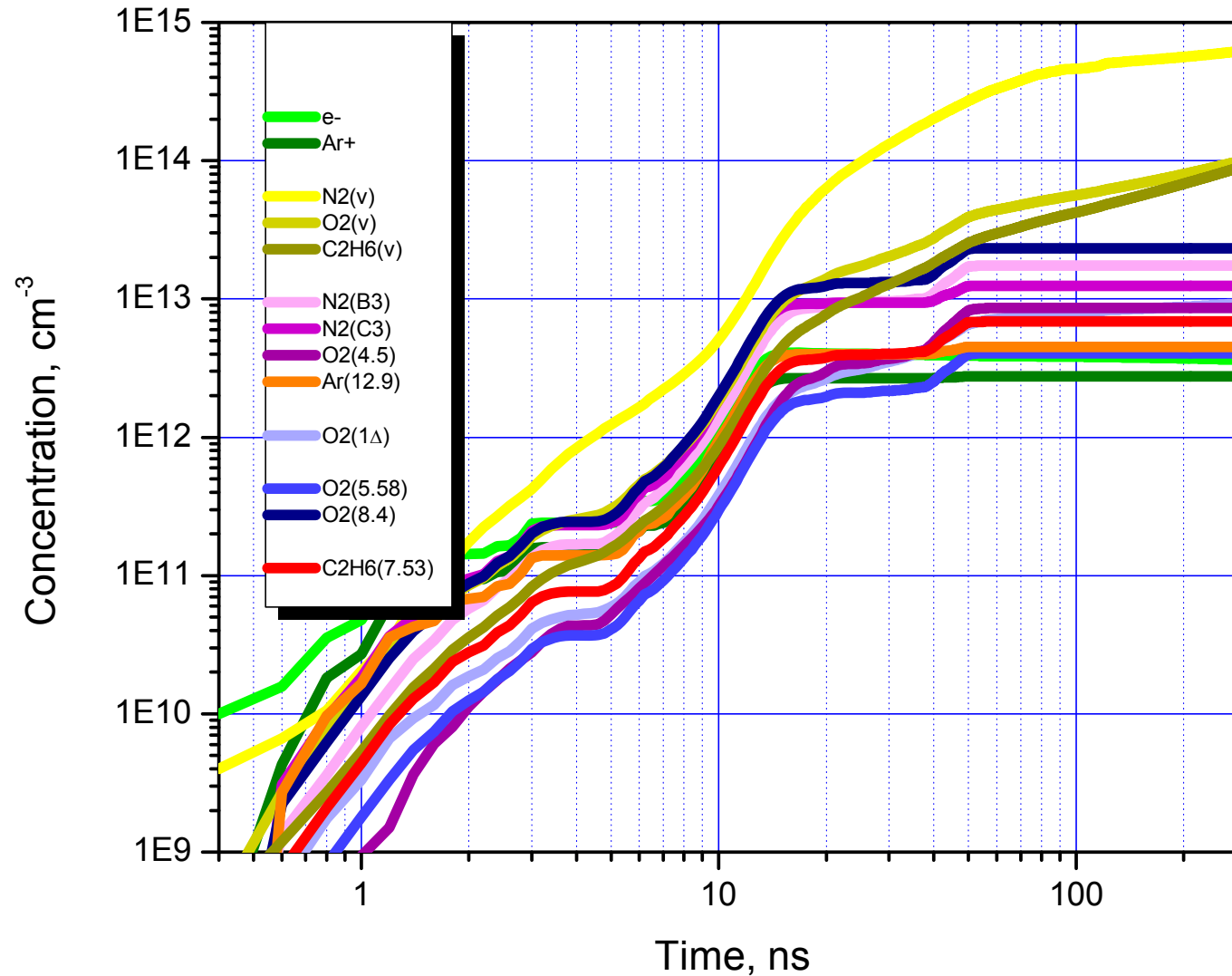


# Discharge Dynamics



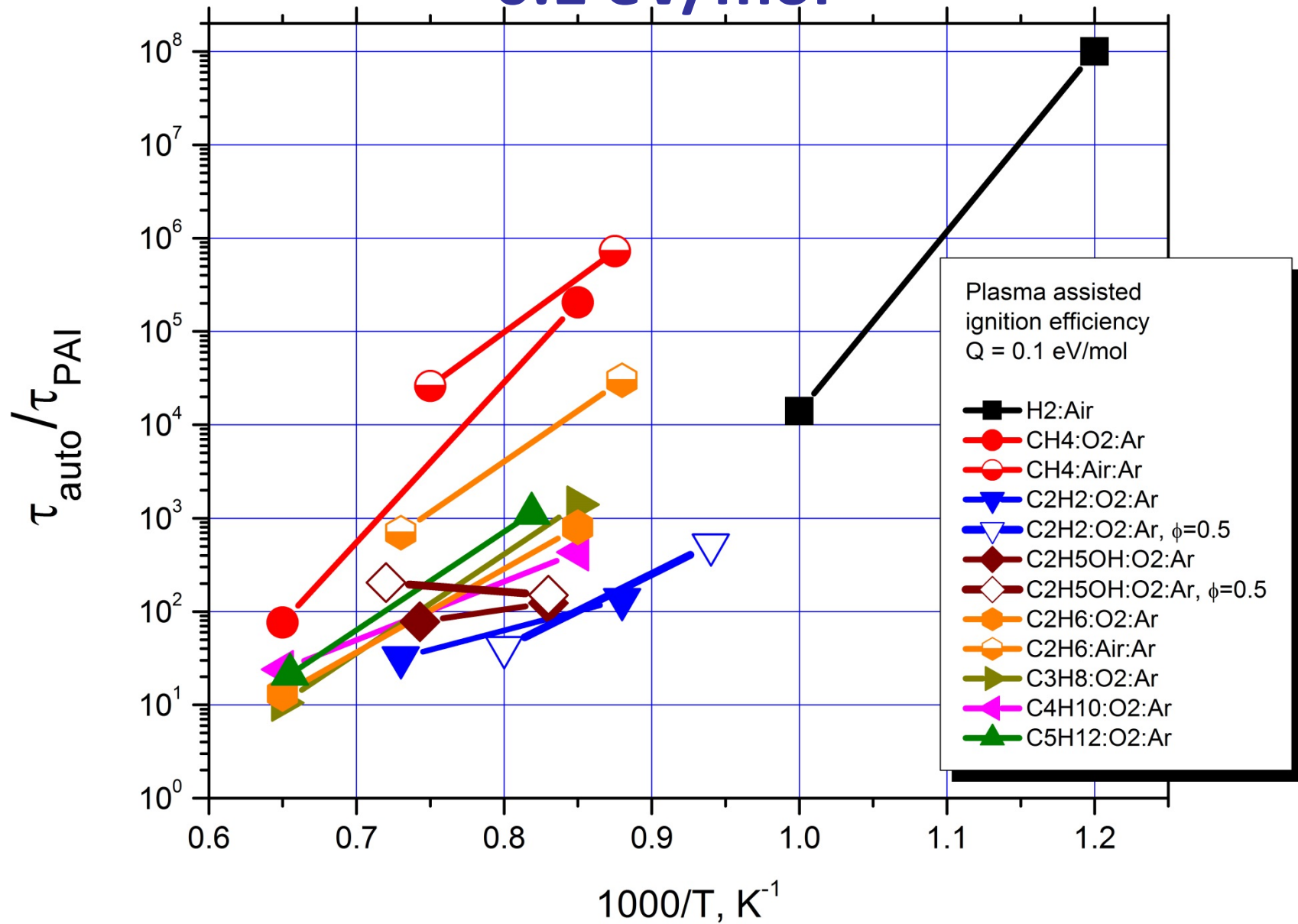
# Active Particle Production – Discharge Phase

$U_s = 943.6 \text{ m/s}$ ;  $P_0 = 17 \text{ Torr}$ ;  $P_5 = 1.04 \text{ atm}$ ;  $T_5 = 1525 \text{ K}$



# Plasma Ignition Sensitivity

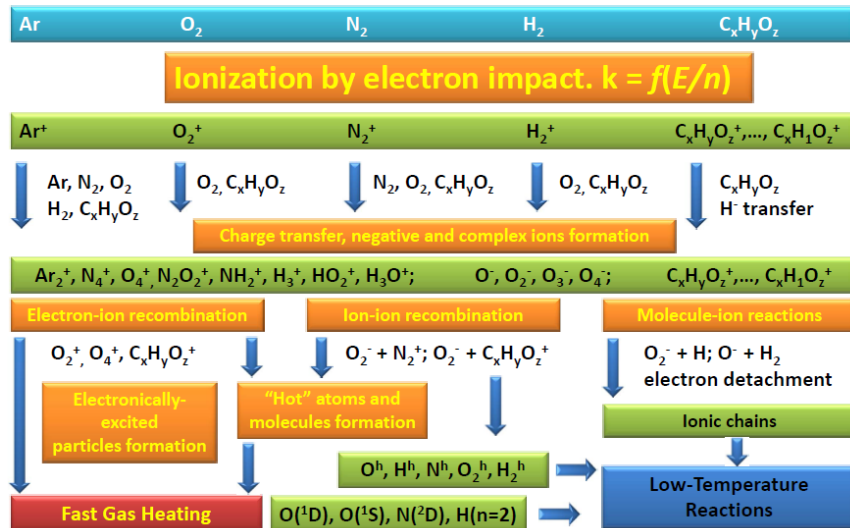
## 0.1 eV/mol





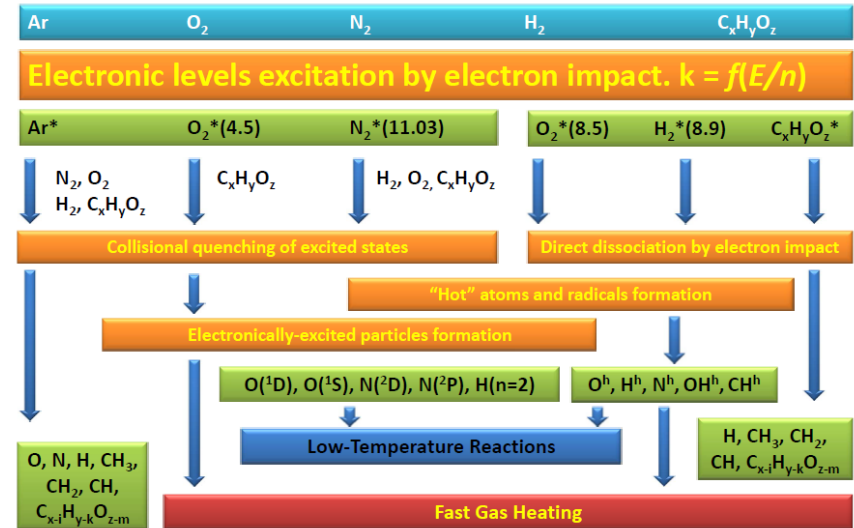
## Princeton Plasma Combustion Kinetics

### Major Pathways



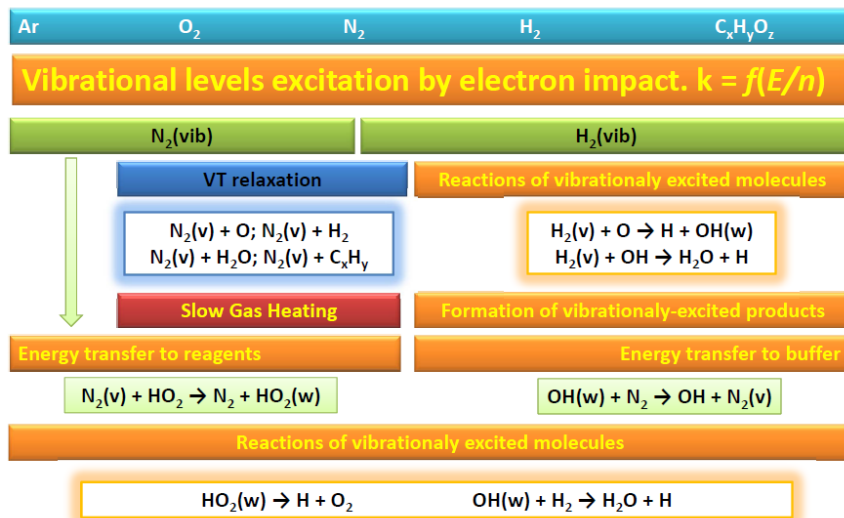
## Princeton Plasma Combustion Kinetics

### Major Pathways



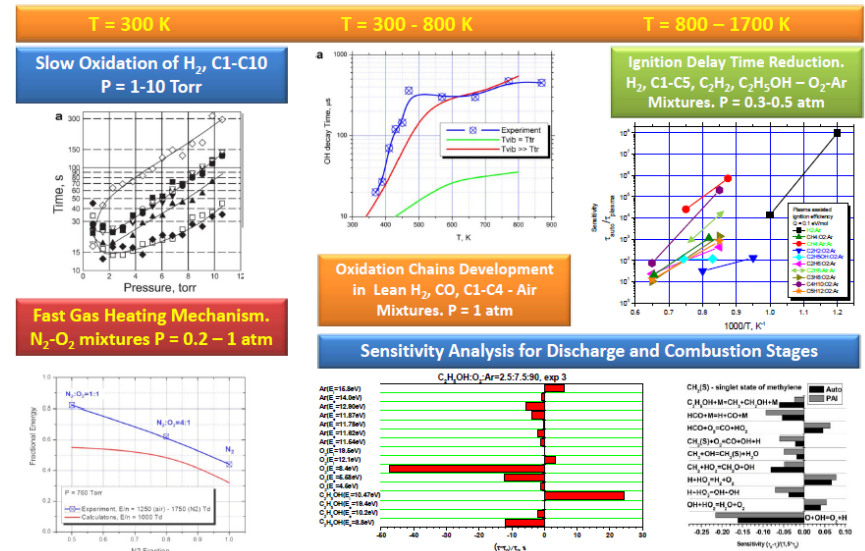
## Princeton Plasma Combustion Kinetics

### Major Pathways



## Princeton Plasma Combustion Kinetics

### Mechanism Validation



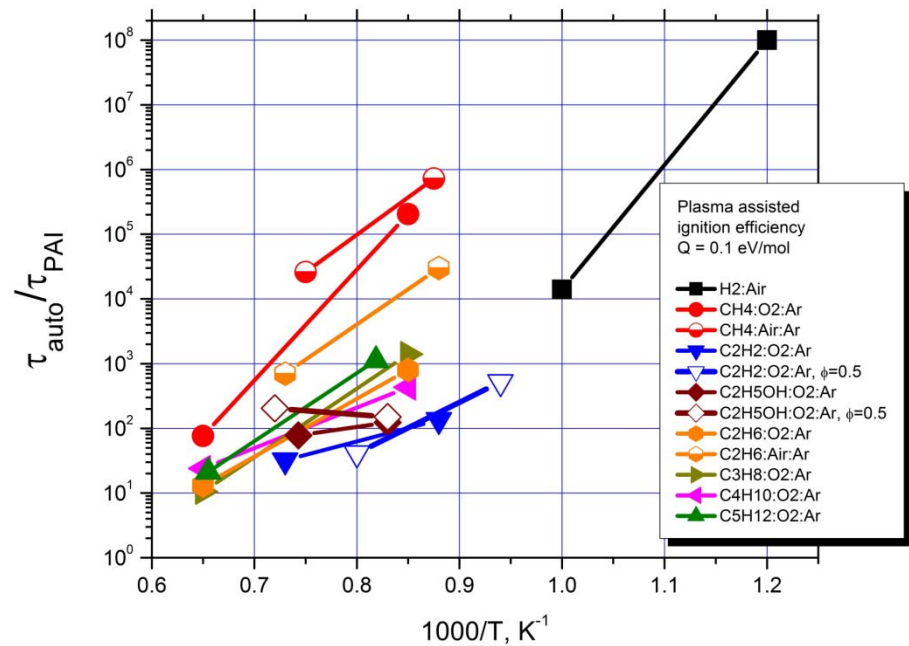
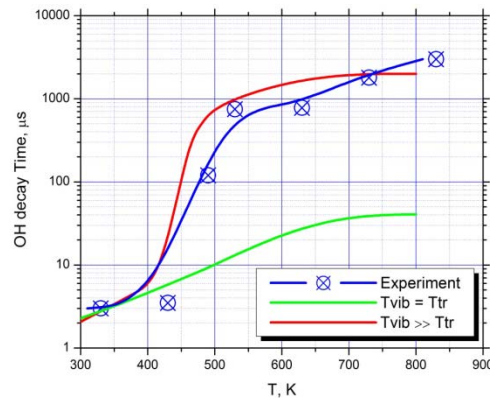
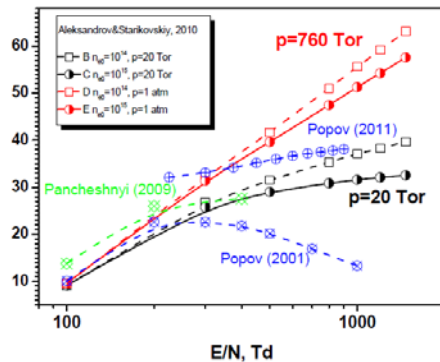
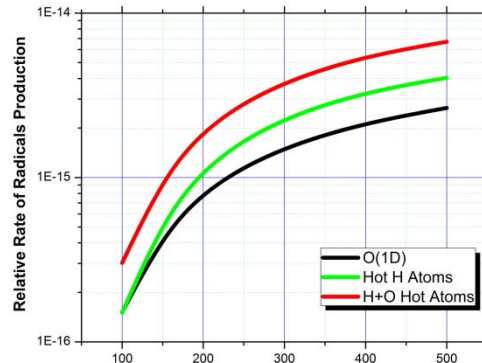
# Other Major Results

## 3 NEW MECHANISMS:

- Radicals Production Increase Due to Translationally Hot Atoms Formation
- Mechanism of Fast Heating in Plasmas at high E/n
- Vibrational Decomposition of Peroxides (HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, etc)

## EXPERIMENTAL DATABASE:

- Plasma Ignition Delay Time database for H<sub>2</sub>, C<sub>1</sub>-C<sub>5</sub>, acetylene, ethylene, ethanol





**The work was supported by**

**AFOSR**  
**Technical Monitor**  
**Dr Chiping Li**



PRINCETON  
University